THE PROPERTIES OF ZEROVALENT NICKEL-CARBONYL-DIPHOSPHINE COMPLEXES AND THEIR APPLICATION TO THE SYNTHESIS OF HETEROBIMETALLIC SYSTEMS

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ABSTRACT

This work involves the investigation of properties of zerovalent Ni-CO-diphosphine complexes and their application to the synthesis of heterobimetallic systems. Two Ni(O)-carbonyl-diphosphine complexes [Ni(CO)(dppe-PP')(dppe-P)] and [$Ni(CO)_2$(dppm-P)$_2$] have been prepared. [Ni(CO)(dppe-PP')(dppe-P)] has been prepared by the reaction of $NiCl_2.6H_2O$ with dppe, $NaBH_4$ and CO. The dicarbonyl species [$Ni(CO)_2$(dppm-P)$_2$] has also been prepared in the same way but here dppm is used instead of dppe.

The complex [Ni(CO)(dppe-PP')(dppe-P)] reacts with MeCOCl, PhCOCl, I_2, HCl gas, air and some alkyl and aryl halides, e.g., MeI, EtI, PhCl, PhBr, $C_6H_{11}Br$. With MeCOCl and PhCOCl it gives no organometallic product but *cis* square planar Ni(II) complex [$NiCl_2$(dppe-PP')] found to be diamagnetic. The complex also reacts with I_2 to give a Ni(II) complex [NiI_2(dppe-PP')]. Protonation of the complex [Ni(CO)(dppe-PP')(dppe-P)] with HCl gas gives a mixture of a nickel hydride complex, possibly [NiH(dppe-PP')$_2$]$^+$ and [$NiCl_2$(dppe-PP')]. With alkyl and aryl halides [Ni(CO)(dppe-PP')(dppe-P)] produces a Ni(O) complex [Ni(dppe-PP')$_2$]. The dicarbonyl species reacts with I_2 to give a mixture of [NiI_2(dppm-PP')] and [NiI_2(dppm-P)$_2$]. In the reactions with air [Ni(CO)(dppe-PP')(dppe-P)] gives no oxidized product but loses CO to give [Ni(dppe-PP')$_2$]. The same reaction with [$Ni(CO)_2$(dppm-P)$_2$] produces a mixture of oxides of dppm, [$Ph_2P(O)CH_2PPh_2$] and [$Ph_2P(O)CH_2P(O)Ph_2$].

[Ni(CO)(dppe-PP')(dppe-P)] and [$Ni(CO)_2$(dppm-P)$_2$] have been applied to the synthesis of heterobimetallic complexes by reaction with [$PdCl_2$(COD)], [$Mo(CO)_3(C_7H_8)$], [$Mo(CO)_3$(MeCN)$_3$], [$Rh_2(\mu\text{-}Cl)_2(CO)_4$] and [$W(CO)_4$(MeCN)$_2$] under nitrogen. A Ni-Pd hetrobimetallic complex [$NiPdCl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2$] has been identified together with a mixture of [$PdCl_2$(dppm-PP')] and [$Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2$] from the reaction of [$Ni(CO)_2$(dppm-P)$_2$] with [$PdCl_2$(COD)] at room temperature. Attempts at reaction of [$Ni(CO)_2$(dppm-P)$_2$] with [$Mo(CO)_3(C_7H_8)$], [$Mo(CO)_3$(MeCN)$_3$] and [$W(CO)_4$(MeCN)$_2$] resulted in dimerization of [$Ni(CO)_2$(dppm-P)$_2$] to [$Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2$]. This structure has been characterized by X-ray crystallography. Reactions of [$PdCl_2$(COD)] and [$Mo(CO)_3(C_7H_8)$] with [Ni(CO)(dppe-PP'(dppe-P)] produce [$NiCl_2$(dppe-PP')] and [Ni(dppe-PP')$_2$] respectively. A mixture of [RhCl(CO)(dppe-PP')], [RhCl(dppe-PP')$_2$] and [Ni(dppe-PP')$_2$] has been obtained from the reaction of [Ni(CO)(dppe-PP'(dppe-P)] with [$Rh_2(\mu\text{-}Cl)_2(CO)_4$]. In the reaction of [$Ni(CO)_2$(dppm-P)$_2$] with [$Rh_2(\mu\text{-}Cl)_2(CO)_4$] a mixture of dirhodium complexes *trans*-[$RhCl(CO)(\mu\text{-}dppm)]_2$ and [$Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2$] has been suggested.

The complexes have been characterized from the results of IR, ^{1}H-NMR, ^{31}P-NMR and UV/visible spectroscopy.

DECLARATION

This dissertation has not been nor is being currently submitted for the award of any other Degree or similar qualification.

A. B. M. SHAMSUR RAHMAN

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DEDICATION

TO

MY PARENTS AND LOVING

DAUGHTER

PRIMA

ABBREVIATIONS

A^0	: angstrom unit (10^{-10} m)
Bu	: butyl group
Bu^t	: tertiary butyl group
cm^{-1}	: wave number
COD	: 1,5-cyclooctadiene
Cy	: cyclohexyl group
dba	: dibenzylideneacetone
δ	: chemical shift in parts per million
d(*i*-Pr)pe	: 1,2-bis(*iso*-propylphosphino)ethane
dmpe	: 1,2-bis(dimethylphosphino)ethane
dmpm	: bis(dimethylphosphino)methane
dppb	: 1,4-bis(diphenylphosphino)butane
dppb-PP'	: chelate dppb
dppe	: 1,2-bis(diphenylphosphino)ethane
dppe-P	: monodentate dppe
dppe-PP'	: chelate dppe
μ-dppe	: bridging bidentate dppe
dppm	: bis(diphenylphosphino)methane
dppm-P	: monodentate dppm
μ-dppm	: bridging bidentate dppm
dppp	: 1,3-bis(diphenylphosphino)propane
dppp-PP'	: chelate dppp
η^5	: hapticity notation; five ligand atoms bonded to metal atom
Et	: ethyl group
Hz	: hertz, S^{-1}

IR	: infrared (for infrared spectra, b = broad, m = medium, s = strong)
i-Pr	: *iso*-propyl group
M	: metal
Me	: methyl group
NMR	: nuclear magnetic resonance (s = singlet d = doublet, b = broad, t = triplet, q = quartet and m = multiplet)
ppm	: parts per million
Ph	: phenyl group
Phen	: 1,10-phenanthroline
Phen-PP'	: chelate Phen
π	: pi bonding orbital
Pr	: propyl group
Py	: pyridine
σ	: sigma bonding orbital
σ^*	: sigma antibonding orbital
THF	: tetrahydrofuran
TMP	: tetramethylphosphate
TMS	: tetramethylsilane
UV	: ultra violet

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SECTION 1

AIMS AND OBJECTIVES

AIMS AND OBJECTIVES

The development of the chemistry of zerovalent nickel has been accompanied by many applications in the field of homogeneous catalysts. Examples include; the dimerization and oligomerization of butadiene, the catalytic addition of hydrogen cyanide to double bonds and isomerization of alkenes. In addition, bridging diphosphine ligands can lock together two metal atoms in close proximity and hence promote organometallic reactions involving two metal centres. Such reactions are often invoked in homogeneous catalysis using binuclear or cluster complex catalysts[1] and many useful models for these reactions can be developed using binuclear phosphine-bridged complexes. For example, the complexes $[Rh_2(CO)_2(\mu\text{-dppm})_2]$ and $[Pd_2Cl_2(\mu\text{-dppm})_2]$ will each add alkynes in the bridging position and they act as catalysts for hydrogenation of ethyne to ethene and cyclotrimerization of alkynes respectively[2-3]. Similarly, the bimetallic complexes $[Rh_2(CO)_2(\mu\text{-S})(\mu\text{-dppm})_2]$, $[Ir_2(CO)_2(\mu\text{-S})(\mu\text{-dppm})_2]$ and $[Ir_2H_2(CO)_2(\mu\text{-S})(\mu\text{-dppm})_2]$ are catalysts for hydrogenation of ethyne and ethene[4].

The most general synthetic route to carbonyl-phosphine complexes of transition metals in zero oxidation states, is to react metal carbonyl complexes with phosphines[5-8]. Recently, an alternative route[9-10] to synthesize these complexes can be found by reduction of metal

salt[9]/phosphine mixtures by $NaBH_4$ in the presence of CO; this serves as both an additional reducing agent and a stabilizing ligand. This method has been shown to be particularly useful for preparing Ni(O) complexes, avoiding the inconvenient use of the metal carbonyl. Therefore, the zerovalent nickel complexes[10] containing carbonyl ligands together with phosphines such as dppm or dppe acting in a monodentate or chelating fashion towards metal ions, [Ni(CO)(dppe-PP')(dppe-P)] and $[Ni(CO)_2(dppm\text{-}P)_2]$ have been prepared. These nickel-carbonyl-diphosphine complexes have enormous potential for study and the aim of this work was to explore the reactivity of these complexes. It was proposed that this would be achieved in the following stages :

(1). It was thought that the zerovalent complexes [Ni(CO)(dppe-PP')(dppe-P)] and $[Ni(CO)_2(dppm\text{-}P)_2]$ should prove to be very reactive towards oxidative addition[11-13]. Oxidative addition is a common reaction in homogeneous catalytic cycles. Related complexes of Pt(O) have been shown to display such reactivity[14]. The initial work, therefore, involved the study of the reactions of [Ni(CO)(dppe-PP')(dppe-P)] and $[Ni(CO)_2(dppm\text{-}P)_2]$ with small molecules of the type H_2, O_2, HCl, I_2, RCOCl and RX (R = Me, Et, Ph, $PhCH_2$ and X = Cl, Br, I). Also, the reactions of the zerovalent nickel complexes with HCl gas were effected in attempts to prepare stable Ni(II) hydride derivatives, which are

of interest in the study of homogeneous hydrogenation and hydrogen transfer reactions[4].

(2). Diphosphine ligands have been widely used to promote the formation of homobinuclear complexes[15-18], but their use in the formation of heterobinuclear systems has not been explored in detail[19]. The second stage of the project, therefore, was to investigate the use of $[Ni(CO)_2(dppm\text{-}P)_2]$ and [Ni(CO)(dppe-PP')(dppe-P)] for the synthesis of heterobimetallic complexes by their reactions with compounds such as $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$, $[Mo(CO)_3(C_7H_8)]$, $[Mo(CO)_3(MeCN)_3]$, $[PdCl_2(COD)]$ and $[W(CO)_4(MeCN)_2]$.

Species were characterized by IR, ^{1}H-NMR, ^{31}P-NMR and UV/visible spectroscopy.

SECTION 2

GENERAL INTRODUCTION

2.1. ZEROVALENT NICKEL COMPLEXES : INTRODUCTION

(a). Zerovalent Nickel Complexes

The discovery of a volatile compound of nickel by C. Langer, during the study of transformation of CO into CO_2 and carbon catalysed by metallic nickel, led to isolation in 1890 of the first coordination compound of the metal in zero oxidation state[20-22], $[Ni(CO)_4]$. The next member of this new class of compounds, $[Fe(CO)_5]$, was discovered independently by Mond[23] and Berthelot[24]. At this time the lack of knowledge on the nature of chemical bonds did not allow any interpretation of the structure of such very unusual derivatives. Even in the first decade of the twentieth century, when Werner's theory, proposed in 1893, had been generally accepted as a new satisfactory key interpreting "complex" compounds this theory was not extended to the metal carbonyls. They were in fact still regarded as anomalous organic compounds, with structures of type :

Figure 1

without any obvious relationship to other known inorganic substances.

Before 1942, the idea of an oxidation number of zero was not taken into serious consideration. In 1942 when $K_4[Ni(CN)_4]$ and $K_4[Pd(CN)_4]$ were obtained[25,26], chemists had to recognize the possibility that a metal in a compound might be in the oxidation state of zero[27]. This view was formally reported by the fact that $K_4[Ni(CN)_4]$ could be obtained by the additive reaction between elemental nickel and potassium cyanide :

$$Ni + 4\ KCN \longrightarrow K_4[Ni(CN)_4]$$

Equation 1

This reaction was analogous to that between nickel(II) cyanide and potassium cyanide :

$$Ni(CN)_2 + 2\ KCN \longrightarrow K_2[Ni(CN)_4]$$

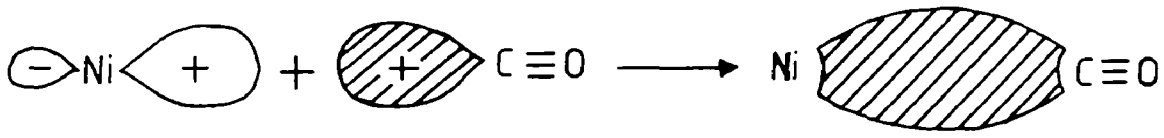
Equation 2

in the course of which none of the atoms changes its oxidation number. The cyanide ion $[:C\equiv N:]^-$ is isoelectronic with carbon monoxide $:C\equiv O:$ and consequently $Ni(CO)_4$ is isoelectric with $[Ni(CN)_4]^{4-}$. This justifies the consideration that metal carbonyls like $Ni(CO)_4$ are neutral coordination compounds with the metal in the zero oxidation state.

(b). Bonding of Ni to CO

The way in which CO engages in bonding to Ni can be explained as follows :

1. First, there is overlap of a filled carbon σ orbital with a σ-type orbital of the Ni metal atom as in figure 2. Here, electron density flows from carbon to nickel. Such a dative overlap would lead to an unacceptable concentration of electron density on the Ni atom. The metal therefore attempts to reduce this electron density by pushing electrons back to the ligand.



Empty σ orbital **Filled σ orbital** **σ-bond**

Figure 2 : The formation of the metal <--- carbon σ bond using an unshared pair of electrons on the C atom. The other orbitals are omitted for clarity.

2. A second dative overlap of a filled $d\pi$ or hybrid metal orbital with the empty, π^* or antibonding $p\pi$ orbital on carbon monoxide as in figure 3 which can act as an acceptor of electron density.

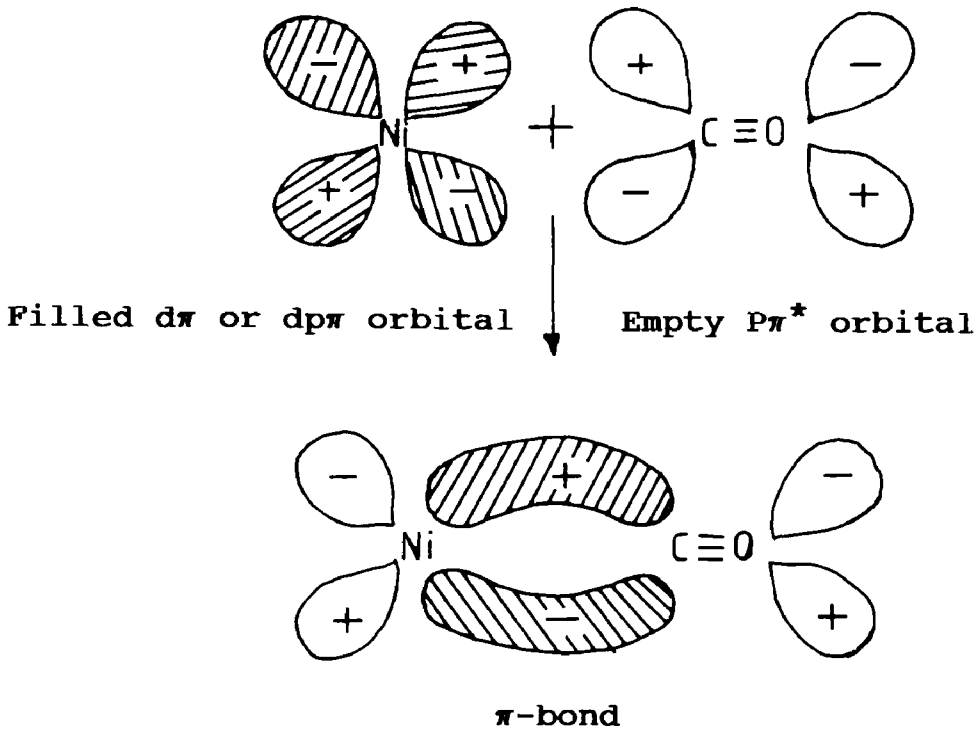


Figure 3 : The formation of the metal ---> Carbon π bond. The other orbitals on the CO are omitted for clarity.

This bonding mechanism is synergic, since the drift of metal electron density, referred to as "Back-Bonding" into CO orbitals will tend to make the CO as a whole negative, hence to increase its basicity via the σ orbital of carbon; at the same time the drift of electrons to the metal in the σ bond tends to make the CO positive, thus enhancing the acceptor strength of the π orbitals. The acceptor properties of the ligand would stabilize Ni in a low oxidation state.

(c). Bonding between Ni and Phosphines

Compounds of the type PX_3 especially when X is relatively electronegative, such as Ph, OR, Cl or F are also effective π acceptor ligands[28].

The occurrence of Ni ⟵ P dative σ bonding is arranged by the overlap of a filled phosphorus σ orbital with a σ-type orbital of Ni resulting the transfer of electrons from P to Ni which leads to an unacceptable concentration of electron density which is back donated to the phosphine.

The occurrence of M ⟶ P dative π bonding is a generally acknowledged fact, the explanation for it entails controversy. The classical and still widely credited, picture is that shown in figure 4 in which

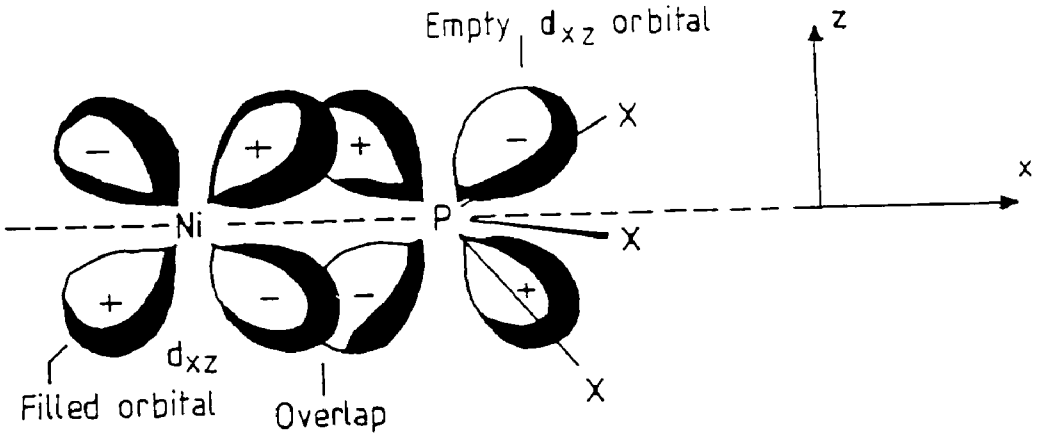


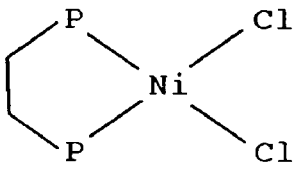
Figure 4 : The back-bonding from a filled metal d orbital to an empty phosphorus 3d orbital in the PPh_3 ligand PX_3 taking the internuclear axis as the Z axis.An exactly similar overlap occurs in the XY plane using the dxy orbitals.

phosphorus specifically employs a pair of its d orbitals to accept metal electrons. However, it has been proposed on the basis of quantum mechanical calculations that phosphorus p orbitals and the P-Ph_3 σ^* (σ^* = antibonding orbital) orbitals may play a major role in accepting metal $d\pi$ electrons[29-32]. Experimental evidence for or against such ideas is lacking.

(d). Dppm and Dppe as Ligands

Tertiary phosphine ligands have played a major role in modern coordination chemistry[33]. These ligands are easy to synthesize and the electronic and steric properties of the ligands can be varied in a systematic way by varying the substituents on phosphorus[34] and by varying the back-bone length. The ligands bind strongly to many transition metals in low oxidation states and are commonly used to stabilize organometallic and hydride derivatives of the elements, either in isolated compounds or as intermediates in homogeneous catalysis.

The recent review[35] on the coordination chemistry of dppm clearly illustrates the ability of this ligand to act in a chelating, monodentate or a bridging fashion towards metal ions. It has long been known that dppe can also act as chelate ligand as in [$NiCl_2$(dppe-PP')] (figure 5).



(for clarity phenyl groups are omitted)

Figure 5 : Structure of $[NiCl_2(dppe\text{-}PP')]$

In forming chelate complexes, the optimum ring size for a metal having natural bond angles at 90 ^{o} to one another is five as in figure 5 and for this reason dppe is known as an excellent chelate[35] ligand. Dppm can chelate[35] (figure 6) but the four membered ring so formed is strained and the ligand has a greater tendency to act either as a monodentate ligand (figure 7a) or as a bridging bidentate[35] ligand (figure 7b).

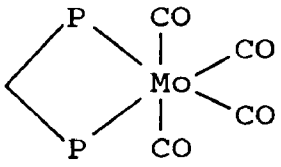


Figure 6 : Structure of *cis*-$[Mo(CO)_4(dppm\text{-}PP')]$

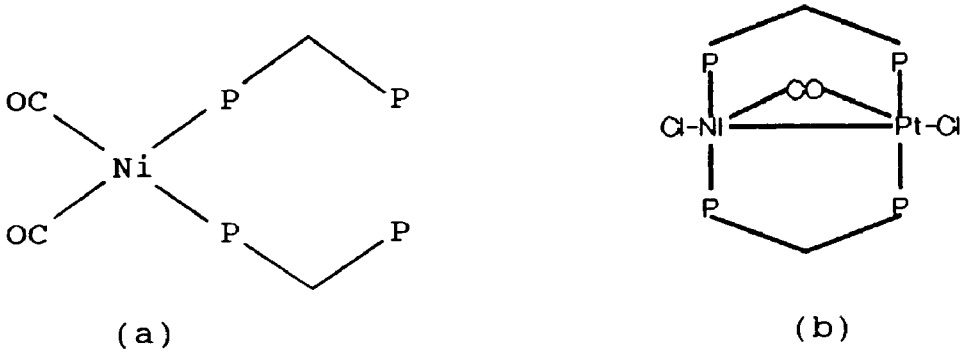


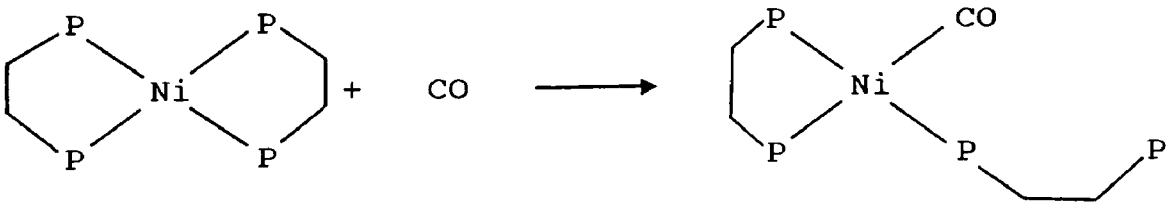
Figure 7 : (a). Monodentate dppm (b) Bridging dppm

(e). Preparation of Ni(O)-CO-Phosphine Complexes

The most general pathway to synthesize carbonyl phosphine complexes of transition metals in low oxidation states now is known to react metal carbonyl complexes with phosphine[5-8]. Several phosphino carbonyl complexes of Ni(O) have been obtained by the reaction of $Ni(CO)_4$ with tertiary phosphines[36] giving products of the type $[Ni(CO)_2(PPh_3)_2]$. When nickel carbonyl is treated with the diphosphines $1,2\text{-}C_6H_4(PR_2)_2$ and $C_2H_4(PR'_2)_2$ (where R = Me, Et and Ph, and R′ = Et and Ph) derivatives of the type[37] $[Ni(CO)_2(diphosphine)]$ are formed.

A less common approach is to treat either already substituted metal carbonyls[38] or metal(O) phosphine complexes[39] with CO. When $[Ni(PPh_3)_4]$ is allowed to react[40] with CO in benzene, $[Ni(CO)_2(PPh_3)_2]$ is rapidly formed, together with a small amount[36,41] of $[Ni(CO)_3(PPh_3)]$.

$[Ni(dppe\text{-}PP')_2]$ reacts[42] with CO in benzene to form $[Ni(CO)(dppe\text{-}PP')(dppe\text{-}P)]$ and a small amount of $[Ni(CO)_2(dppe\text{-}PP')]$.

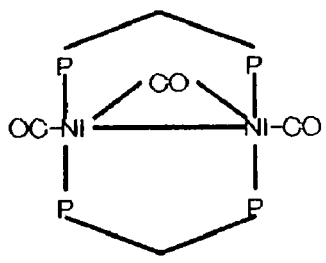


Equation 3

A recent publication[10] has shown that there is an alternative route for the synthesis of Ni(O) complexes containing carbonyl ligands together with monodentate or chelating phosphines such as dppm or dppe. The synthesis is achieved by the reduction of saturated CO solutions of Ni(II)[9] salts and phosphines such as PPh_3 or $Ph_2P(CH_2)_nPPh_2$ (n = 1, dppm; n = 2, dppe) by $NaBH_4$ or $NaBH_3CN$, where CO serves as both an additional reducing agent and a stabilizing ligand[43]. This method has been shown to be particularly useful for preparing Ni(O) complexes, avoiding the inconvenient use of the metal carbonyl.

(i). The Reaction[9] of Ni(II) chloride with dppm, $NaBH_3CN$ and CO

The reaction between $NiCl_2.6H_2O$, dppm and $NaBH_3CN$ (a milder reducing agent[44] than $NaBH_4$) leads to a Ni(I)-cyanide-dppm complex[45]. In the presence of CO a variety of Ni(O)-CO-dppm complexes are formed. Thus, yellow-orange crystals[9] of $[Ni_2(CO)_2((\mu\text{-}CO)(\mu\text{-dppm})_2]$ have been obtained, the formula of which suggests an A-frame structure with a Ni-Ni bond to achieve an 18-electron count on each Ni atom.

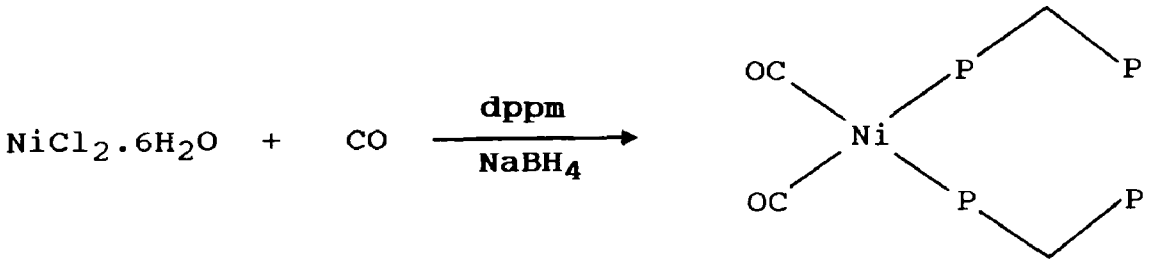
$NiCl_2.6H_2O$ + dppm $\xrightarrow[CO]{NaBH_3CN}$ 

Equation 4

(ii). Syntheses[10] of [Ni(CO)(dppe-PP')(dppe-P)] and $[Ni(CO)_2(dppm\text{-}P)_2]$

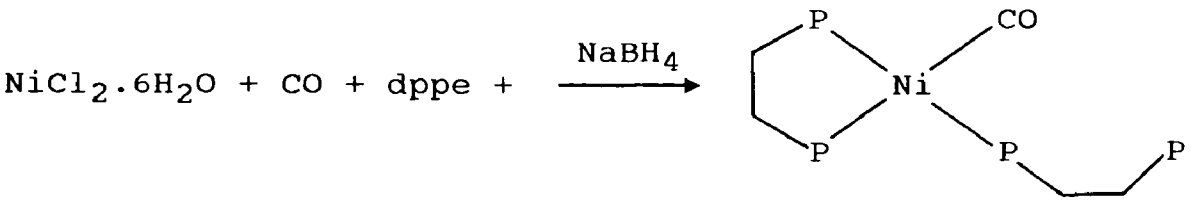
When $NiCl_2.6H_2O$ reacts with PPh_3, in the presence of CO, the major product is $[Ni(CO)_2(PPh_3)_2]$ (i.e. the same product as from the reaction of $Ni(CO)_4$ with PPh_3), but with the bis(phosphines), metal-CO-phosphine complexes containing monocoordinate phosphine ligands are produced.

The $NiCl_2.6H_2O$/dppm/CO/$NaBH_4$ system yields[10] colourless crystals of tetrahedral $[Ni(CO)_2(dppm\text{-}P)_2]$ which rapidly rearranges in solution (unless the solution is cooled or an excess of free dppm is present) to give[9,46-47] $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$.



Equation 5

Similarly, the $NiCl_2.6H_2O$/dppe/CO/$NaBH_4$ system where dppe has been used instead of dppm produces[10] [Ni(CO)(dppe-PP')(dppe-P)] (equation 6).



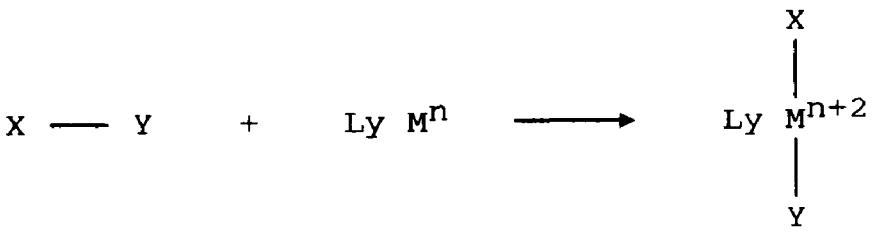
Equation 6

2.2. REACTIVITY OF ZEROVALENT NICKEL COMPLEXES

(a). Oxidative Addition and Reductive Elimination Reactions

(i). Oxidative Addition

An example of oxidative addition is shown by the following equation :



(n = oxidation state of metal, M, Ly = other ligands, X-Y = H_2, MeI, I_2 for example)

Equation 7

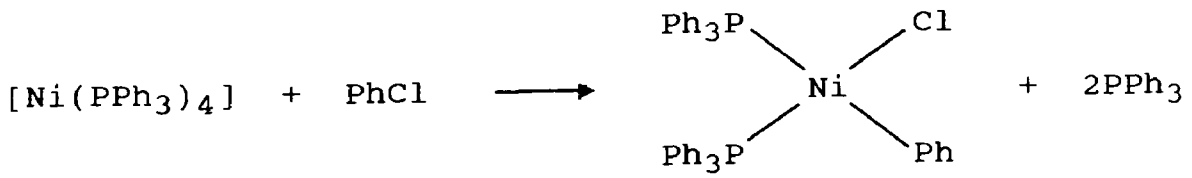
For an oxidative addition reaction to proceed, the metal must have :

(a). Two vacant coordination sites on the complex LyM to allow for the formation of two new bonds to X and Y

(b). Two stable oxidation states separated by two units.

The lower oxidation state should normally exhibit a lower coordination number than the higher one and preferably be coordinatively unsaturated.

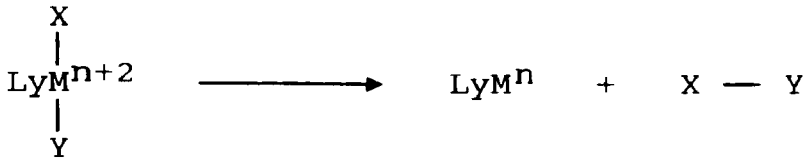
The most studied reactions for transition metals are those of complexes of metals with the d^8 and d^{10} electron configuration, notably Fe^O, Ru^O, Os^O, Rh^I, Ir^I, Ni^O, Pd^O, Pd^{II}, Pt^O and Pt^{II}. However, compounds with eighteen electrons can not normally undergo oxidative addition reactions without expulsion of a ligand. For example $[Ni(PPh_3)_4]$ undergoes an oxidative addition reaction with PhCl :



Equation 8

(ii). Reductive Elimination

Reductive elimination is the reverse of oxidative addition as shown in equation 9.



Equation 9

In reductive elimination reaction, the oxidation number of the metal decreases by two and the coordination number also decreases by two.

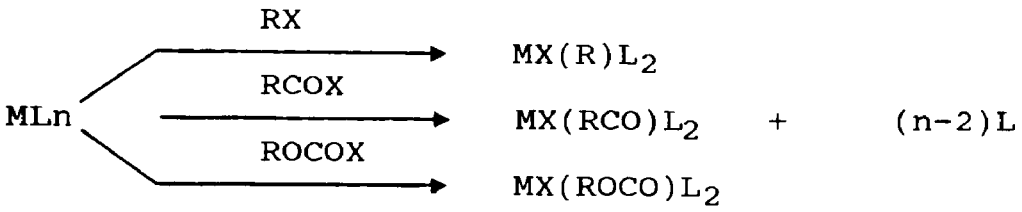
(b). Oxidative Addition Reactions of Zerovalent Nickel Complexes

Some examples of the oxidative addition reactions of Ni(O) complexes are given as follows :

(i). Oxidative Addition of Alkyl halides, Acyl halides, Aryl halides and Alkoxycarbonyl to Ni(O) Complexes

A large number of these oxidative addition reactions have been studied over many years[26] and they are very

useful for the synthesis of metal(II) complexes, according to the following reactions (equation 10).

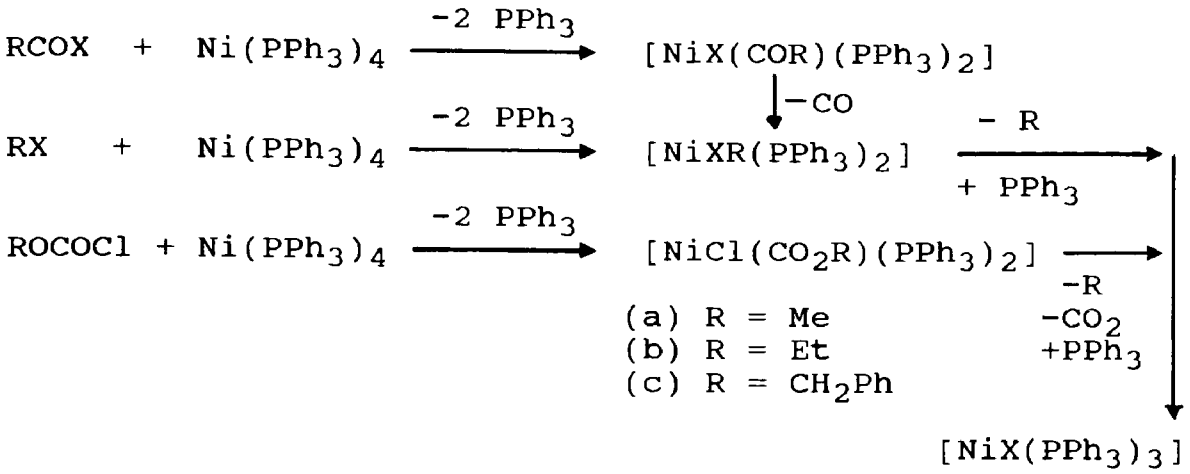


(Here, n = no. of ligands, R = alkyl or aryl group)

Equation 10

Oxidative addition[11] of haloformate and acyl halides to $[Pd(CNBut)_2]$, $[Pd(PPh_3)_4]$, $[Ni(CNBut)_4]$ and $[Ni(PPh_3)_4]$ give ROCO-, RCO- and R-Pd(II)[48] or Ni(II) complexes.

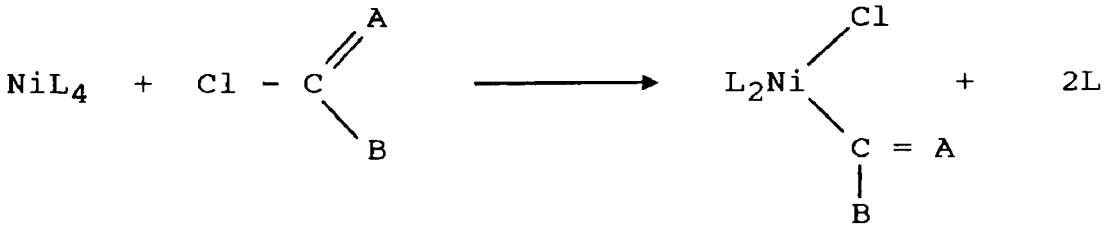
The zerovalent nickel complex[11] $[Ni(PPh_3)_4]$ reacts with ROCOCl (R = Me, Et, CH_2Ph) and RCOX (or RX) (R = alkyl, Ar, X = Cl, Br, I) to give the Ni(II) products $[NiCl(CO_2R)(PPh_3)_2]$ and $[NiXR(PPh_3)_2]$ respectively. The products $[NiCl(CO_2R)(PPh_3)_2]$ and $[NiXR(PPh_3)_2]$ lose RCO_2 and R groups respectively to form the Ni(I) species[11] $[NiX(PPh_3)_3]$. These reactions are shown in equation 11.



Equation 11

(d) X = Cl
(e) X = Br
(f) X = I

Some other oxidative addition reactions of RCOCl and thioacyl RCSCl derivatives to nickel(O) compounds have been reported according to the following scheme[49] :

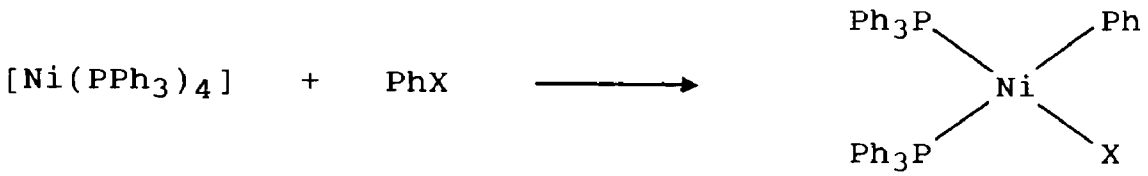


(L = PPh_3, $P(OPh_3)_3$, L_2 = dppp-PP', dppb-PP'; A = O, S; B = Ph, NMe_2)

Equation 12

(ii). Oxidative Addition of Aryl Halides to $[Ni(PPh_3)_4]$

The Ni(O) complex $[Ni(PPh_3)_4]$ undergoes oxidative addition reactions with PhX (X = I, Br, Cl) in the presence of excess PPh_3 to give[50-51] $[NiXPh(PPh_3)_2]$.



Equation 13

Stable aryl nickel(II) complexes of the type $[NiX(aryl)(PPh_3)_2]$ (X = Cl, Br) are prepared by the oxidative additions[52] of aryl halides to $[Ni(PPh_3)_4]$ where aryl is not only a phenyl but also 2-substituted, 3- or 4-substituted (C_6H_4Me) aromatic ligand[12].

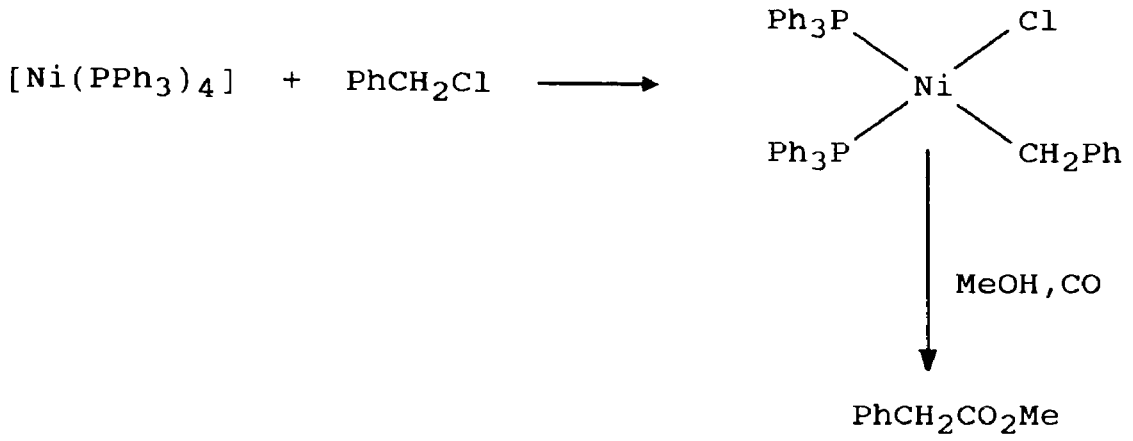
$$[Ni(PPh_3)_4] + Ar\text{-}X \longrightarrow [NiX(Ar)(PPh_3)_2]$$

(Ar = aryl, X = Cl or Br)

Equation 14

(iii). Oxidative Addition of benzyl halides to $[Ni(PPh_3)_4]$

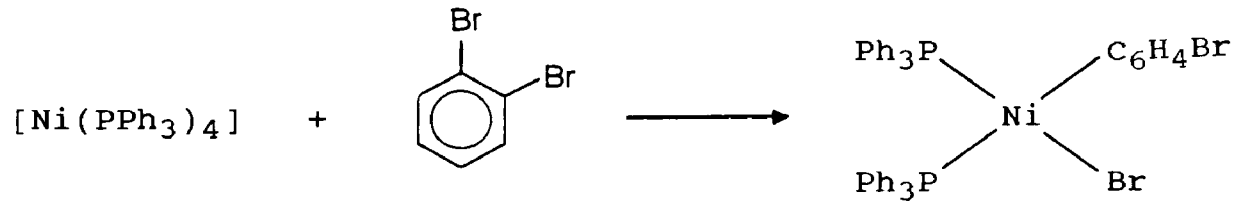
Oxidative addition of benzyl chloride, $PhCH_2Cl$, to $[Ni(PPh_3)_4]$ gives[13] $[NiCl(CH_2Ph)(PPh_3)_2]$ which followed by carbonylation and the addition of MeOH yields $PhCH_2CO_2Me$ (equation 15).



Equation 15

(iv). Oxidative Addition of a dihalosubstituted benzene to [Ni(PPh$_3$)$_4$]

The zerovalent nickel complex [Ni(PPh$_3$)$_4$] undergoes oxidative addition by 1,2-dibromobenzene leading to the organometallic derivative[53] [NiBr(2-C$_6$H$_4$Br)(PPh$_3$)$_2$].

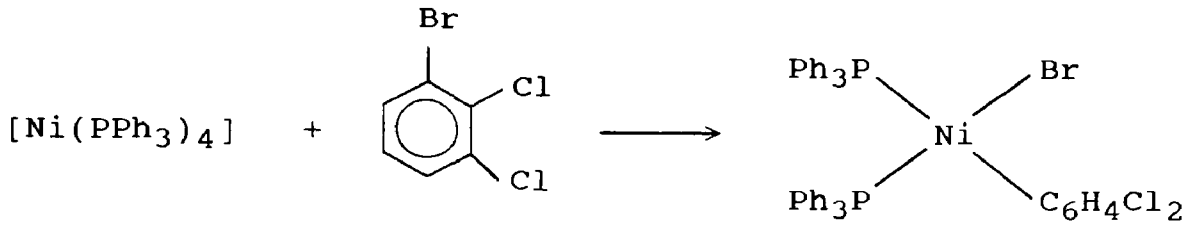


Equation 16

(v). Oxidative Addition of Halopolychlorobenzenes to [Ni(PPh$_3$)$_4$]

(Polychlorophenyl)nickel(II) complexes[54] of the type [NiBrR(PPh$_3$)$_2$], where R = C$_6$H$_n$Cl$_{5-n}$, (2,3-, 2,4-, 2,5, 3,4-, 3,5-dichlorophenyl) are obtained by oxidative

addition of halopolychlorobenzenes RX (R = $C_6H_nCl_{5-n}$, X = Br) to $[Ni(PPh_3)_4]$(equation 17).

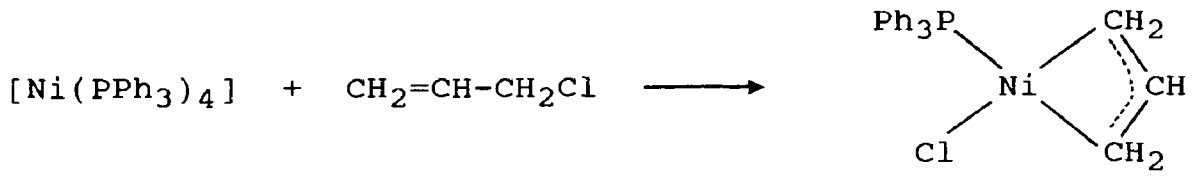


Equation 17

Thus, 2,4-, 2,5-, 3,4- and 3,5-dichlorobenzene derivatives can be prepared.

(vi). Reaction of $[Ni(PPh_3)_4]$ with allyl halides

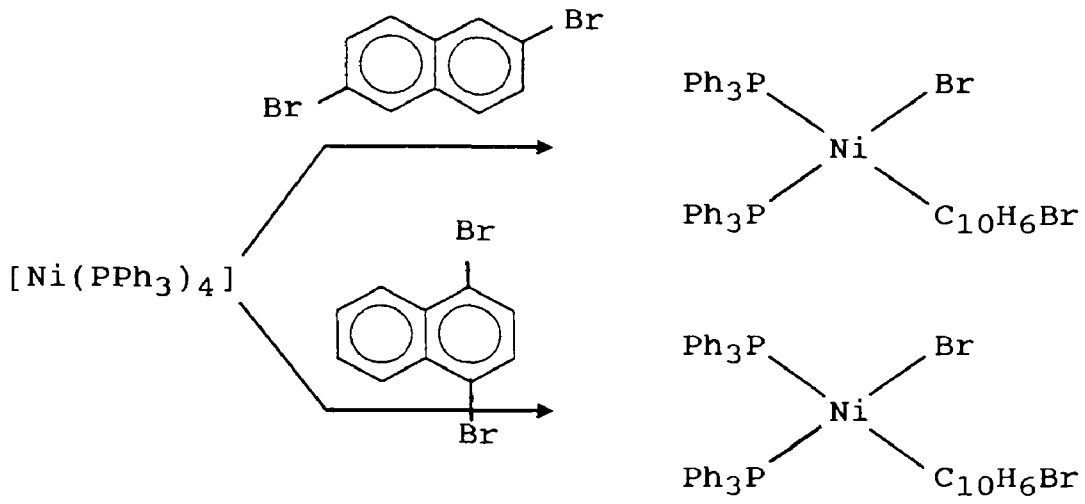
$[Ni(PPh_3)_4]$ undergoes oxidative addition with allyl halides to give organo nickel(II) derivatives[55]; $[NiCl(\eta^3\text{-}C_3H_5)(PPh_3)]$ (equation 19).



Equation 18

(vii). Reaction of 1,4- and 2,6-dibromonapthalene with $[Ni(PPh_3)_4]$

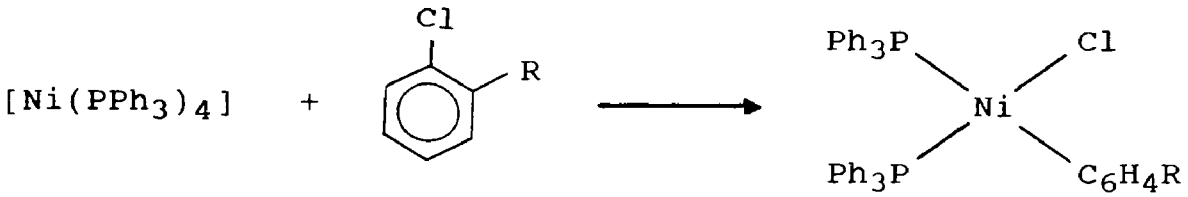
Oxidative addition of 1,4- and 2,6-dibromonapthalene to $[Ni(PPh_3)_4]$ give[56] $[NiBr(4\text{-}C_{10}H_6Br)(PPh_3)_2]$ and $[NiBr(6\text{-}C_{10}H_6Br)((PPh_3)_2]$



Equation 19

(viii). Oxidative Addition of chlorofluorobenzene and chloromethylbenzene to $[Ni(PPh_3)_4]$

$[Ni(PPh_3)_4]$ undergoes oxidative addition with chlorofluoro and chloromethyl benzene to give[57] $2\text{-}C_6H_4F$ and 2-tolyl nickel complexes, $[NiCl(2\text{-}C_6H_4F)(PPh_3)_2]$ and $[NiCl(2\text{-}C_6H_4Me)(PPh_3)_2]$ respectively (equation 20).



(R = F, Me)

Equation 20

(ix). Reactions of Organic halides with $[Ni(PCy_3)_2]$

The reactions[58] of bis(tricyclohexylphosphine)nickel(O), $[Ni(PCy_3)_2]$, with organic halides RX (R = Me, X = I; R = Pr, X = Br; R = Et, X = Br, I; R = Ph, X = Cl) all involve fission of the R-X bond and oxidative addition of the bromides produces the stable complexes $[NiBr(PCy_3)_2]$ and $[NiBrH(PCy_3)_2]$ formed from ß-elimination of hydrogen from $[NiBrR(PCy_3)_2]$ (R = Et) (equation 21).

$$[Ni(PCy_3)_2] + RBr \longrightarrow [NiBrR(PCy_3)_2]$$

$$[NiBrR(PCy_3)_2] \longrightarrow [NiBr(PCy_3)_2] + R^{\bullet}$$

$$[NiBrR(PCy_3)_2] \xrightarrow[\text{of Hydrogen}]{\text{ß-elimination}} [NiBrH(PCy_3)_2] + CH_2{=}CH_2$$

Equation 21

(x). Reaction of 2-chloromethylbenzene with $[Ni(PCy_3)_4]$

$[NiCl(2\text{-}C_6H_4Me)(PCy_3)_2]$ is produced[59] by the oxidative addition of 2-chloromethylbenzene to $[Ni(PCy_3)_4]$. $[NiCl(2\text{-}C_6H_4F)(PCy_3)_2)$ can also be prepared by the same

way using 2-fluorochlorobenzene instead of ClC_6H_4Me (equation 22). $[Ni(PCy_3)_4]$ is produced in the reaction of $Ni(COD)_2$ with PCy_3.

(R = Me, F)

Equation 22

(xi). Reaction of PhCl and RCOX (X = Cl, Br) to $[NiMe_2(dppe\text{-}PP')]$ and $[NiMe_2(dppp\text{-}PP')]$

Addition[60] of PhCl to $[NiMe_2(dppe\text{-}PP')]$ gives [NiClMe(dppe-PP')]and interaction of RCOX (R = alkyl, aryl) with $[NiMe_2(dppe\text{-}PP')]$ and $[NiMe_2(dppp\text{-}PP')]$ gives $[NiXRL_2]$ (L_2 = dppe-PP', dppp-PP' and X = Cl, Br)

$[NiMe_2(dppe\text{-}PP')] + PhCl \longrightarrow [NiClMe(dppe\text{-}PP')]$

$[NiMe_2(dppe\text{-}PP')] + RCOX \longrightarrow [NiXR(dppe\text{-}PP')] + Me_2CO$

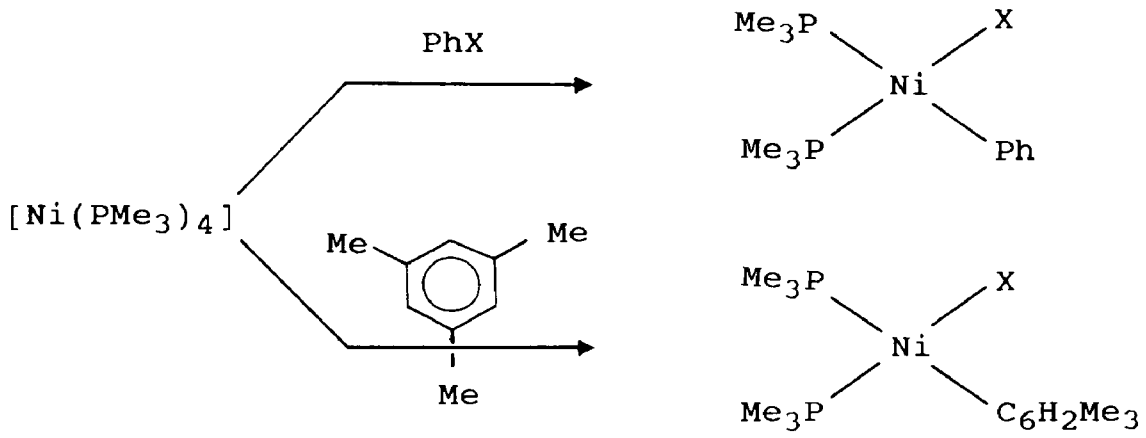
$[NiMe_2(dppp\text{-}PP')] + RCOX \longrightarrow [NiXR(dppp\text{-}PP')] + Me_2CO$

Equation 23

(xii). Reaction of PhX and 2,4,6-trimethylhalobenzenes with $[Ni(PMe_3)_4]$

Reaction[61] of PhX and 2,4,6-trimethylhalobenzenes to $[Ni(PMe_3)_4]$ gives products *trans*-$[NiXPh(PMe_3)_2]$ and

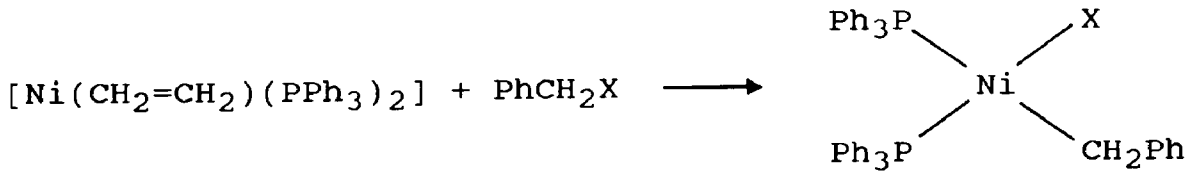
trans-[NiX(2,4,6-$C_6H_2Me_3$)(PMe_3)$_2$] (X = Cl, Br) respectively.



Equation 24

(xiii). Oxidative Addition of benzyl halides to [Ni(C_2H_4)(PPh_3)$_3$]

Oxidative addition of benzyl halides to [Ni(C_2H_4)(PPh_3)$_2$] gives[62] [NiX(CH_2Ph)(PPh_3)$_2$] (X = Br, Cl).



Equation 25

(xiv). Oxidative Addition of 1,4-dihalides to $[Ni(C_2H_4)(PPh_3)_2]$

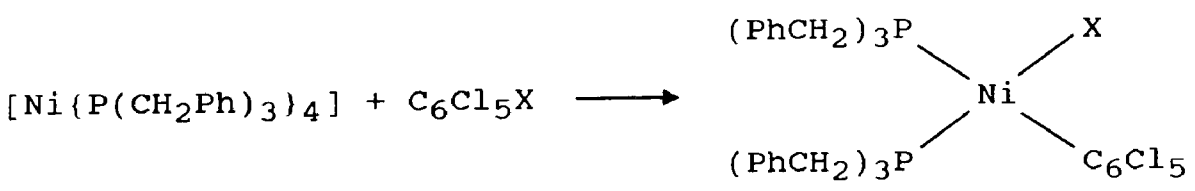
$[1,4\text{-}\{NiClCH_2(PPh_3)_2\}_2C_6H_4]$ is prepared by the reaction[63] of $[Ni(CH_2{=}CH_2)(PPh_3)_2]$ with $[1,4\text{-}(ClCH_2)_2C_6H_4]$ in Et_2O at -20 ^0C (equation 26) whereas with $1,2\text{-}(BrCH_2)_2C_6H_4$, $[NiBr_2(Ph_3P)_2]$ and $C_{16}H_{16}$ are formed.

$$2[Ni(CH_2{=}CH_2)(PPh_3)_2] + 1,4\text{-}(ClCH_2)_2C_6H_4 \longrightarrow [NiClCH_2(PPh_3)_2]_2C_6H_4$$

Equation 26

(xv). Oxidative Addition of pentachlorophenylhalides to $[Ni\{P(CH_2Ph)_3\}_4]$

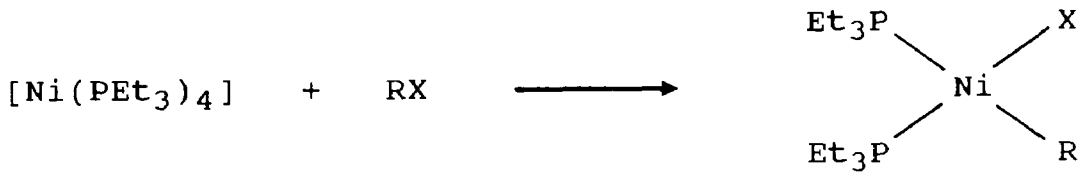
Stable $[NiX(C_6Cl_5)\{P(CH_2Ph)_3\}_2]$ (X = Cl, Br) are prepared[64] by the oxidative addition reactions of pentachlorophenylhalides (X = Cl, Br) with $[Ni\{P(CH_2Ph)_3\}_4]$.



Equation 27

(xvi). Oxidative Additions of aryl, vinyl and acyl halides to $[Ni(PEt_3)_4]$

Aryl, vinyl and acyl halides (RX), but not alkyl halides, react with $[Ni(PEt_3)_4]$ to yield square-planar *trans*-$[NiXR(PEt_3)_2]$ complexes[65] (R = alkyl, aryl and acyl groups, X = halogens) (equation 28).



Equation 28

(xvii). Oxidative Addition of aryl halides to $[Ni(PEt_3)_4]$

Oxidative addition of aryl halides to $[Ni(PEt_3)_4]$ affords[66] *trans*-arylnickel(II) species, together with paramagnetic Ni(I) halides as side products.

$$[Ni(PEt_3)_4] + PhX \longrightarrow \textit{trans}\text{-}[NiXPh(PEt_3)_2]$$

(X = Cl, Br, I)

Equation 29

(xviii). Reactions of $[Ni\{P(i\text{-}Pr_3)\}_4]$ with Methyl halides

Oxidative addition of methyl halides, MeX (X = Cl, Br, I) to $[Ni\{P(i\text{-}Pr_3)\}_4]$ give the products[67] *trans*-$[NiXMe\{P(i\text{-}Pr_3)\}_2]$, which on treatment with PPh_3, give $[NiX(PPh_3)_3]$ (equation 30).

$$[Ni\{P(i\text{-}Pr_3)\}_4] + MeX \longrightarrow \textit{trans}\text{-}[NiXMe\{P(i\text{-}Pr_3)\}_2] \xrightarrow{PPh_3} [NiX(PPh_3)_3]$$

Equation 30

(xix). Oxidative addition of PhCOCl to $[Ni(dppp\text{-}PP')_2]$

$[Ni(dppp\text{-}PP')_2]$ reacts[68] with benzoyl chloride at room temperature in benzene giving the following reaction :

$$[Ni(dppp\text{-}PP')_2] + PhCOCl \longrightarrow [NiCl(COPh)(dppp\text{-}PP')]$$

Equation 31

(c). Reactions of Zerovalent Phosphine Complexes of Ni, Pd and Pt with molecular Oxygen

Molecular oxygen reacts with transition metal complexes containing phosphine ligands in low oxidation states.

These reactions produce a three membered metal-oxygen ring[69] and phosphine oxides.

Triphenylphosphine complexes of nickel(O), palladium(O) and platinum(O) react with molecular oxygen to give the following products[70-74] (equation 32).

$$[M(PPh_3)_4] + 2\ O_2 \longrightarrow [M(O_2)(PPh_3)_2] + 2\ OPPh_3$$
$$(M = Ni, Pd, Pt)$$

Equation 32

The stability of the metal adducts $[M(O_2)(PPh_3)_2]$ (M = Ni, Pd, Pt) follows the order Pt > Pd > Ni. The nickel adduct decomposes above -35 ^{0}C while the palladium derivative slowly decomposes above 20 ^{0}C. The platinum adduct is much more stable, and decomposes at nearly 120 ^{0}C.

For all metals, decomposition eventually leads to the formation of the metal and triphenylphosphine oxide[70].

It has been reported[9] that $[Ni_2(CO)_3(dppm\text{-}P)_3]$ is very reactive towards a trace amounts of oxygen and forms the monoxide of dppm.

(d). Protonation Reaction of Zerovalent Nickel Complexes

Protonation of zerovalent nickel complexes has been achieved by their reaction with hydrogen containing acids. Both four and five coordinate stable nickel hydride complexes have been found in the literature[69,75-77].

$[Ni(PCy_3)_2]$ has been shown[78-79] to react with acids such as HCl, MeCOOH and phenol to form hydridonickel complexes having the composition $[NiHRL_2]$ (R = MeCOO, Cl).

The protonation of zerovalent nickel complexes[75] can be achieved by the addition of strong acids such as HCl, H_2SO_4 and CF_3COOH. For example, protonation of $[Ni\{P(OEt_3)\}_4]$ in benzene, acetone or chloroform leads to five coordinate $[NiH\{P(OEt)_3\}_4]^+$. Analogous nickel complexes of trimethylphosphite give similar results (equation 33).

$$[Ni\{P(OMe)_3\}_4] + HX \longrightarrow [NiH\{P(OMe)_3\}_4]^+ + X^-$$

(HX = HCl, H_2SO_4, CF_3COOH)

Equation 33

Addition of HCl gas to $[Ni(dppe\text{-}PP')_2]$ has been reported by R. A. Schunn[76]. This reaction gives a stable five coordinate nickel hydride complex.

$$[Ni(dppe\text{-}PP')_2] + HCl + AlCl_3 \longrightarrow [NiH(dppe\text{-}PP')_2]AlCl_4$$

Equation 34

Similar protonation reactions have also been shown to be possible[76] with HBF_4.

The stable nickel hydride complexes[77] *trans*-$[NiHX(PCy_3)_2]$ and *trans*-$[NiHX(P(i\text{-}Pr_3))_2]$ (X = halide, SCN or CN) are prepared by the addition of HX, HSCN or HCN to $[Ni(PCy_3)_2]$ and $[Ni(P(i\text{-}Pr_3))_2]$ respectively.

The protonation of zerovalent nickel complexes of the type NiL_4 by acid leads to the formation of a stable five coordinate nickel hydride complex according to the following reaction[69] :

$$H^+ + NiL_4 \longrightarrow [NiHL_4]^+$$

(L = $P(O\text{-}4\text{-}C_6H_4OMe)_3$, $P(O\text{-}4\text{-}C_6H_4Me)_3$, $P(OMe)_3$, $P(O(CH_2)_2Cl)_3$, $P(OEt)_3$, $PPh(OEt)_2$, PMe_3)

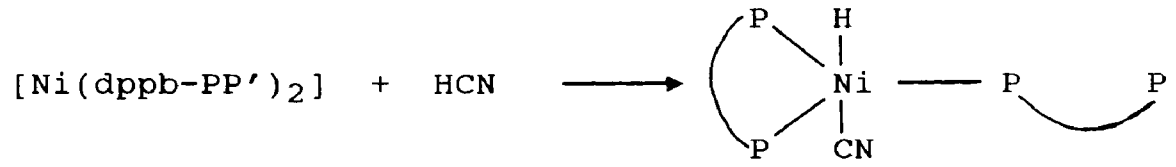
Equation 35

Addition of HCN to zerovalent nickel complexes NiL_4 (L = phosphorus containing ligands) gives a class of five coordinate nickel hydride complexes[80], $[NiHCNL_3]$.

(L = PEt_3, $P(MePh_2)$, $P(OMePh_2)$

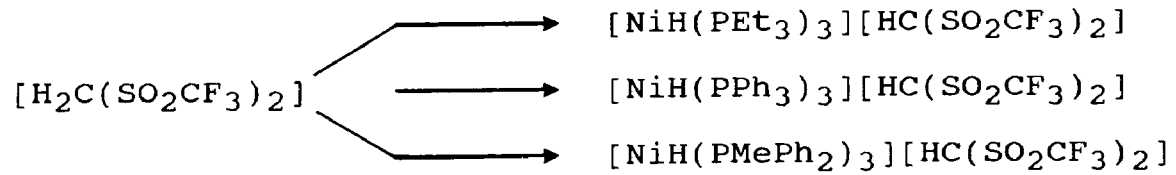
Equation 36

Five coordinate hydrido cyanides can also be formed by the oxidative addition of HCN to $[Ni(dppb\text{-}PP')_2]$.



Equation 37

Protonation of phosphine complexes of zerovalent nickel with $[H_2C(SO_2CF_3)_2]$ yields[81] a $[NiHL_3]^+[HC(SO_2CF_3)_2]$, where L = PPh_3, $P(MePh_2)$, PEt_3.



Equation 38

SECTION 3

METHODS AND MATERIALS

3.1. Schlenk Apparatus

Most of the complexes synthesized and reported in this thesis were air sensitive and sensitivity to oxygen was usually greater in solution than in the solid state. Therefore, all reactions were carried out under vacuum or in a nitrogen atmosphere using a "Schlenk-type Apparatus" (figure 8).

The Schlenk apparatus (figure 8) consisted of two glass tubes, one connected to a nitrogen supply and the other connected to a vacuum pump. They were fitted with glass taps A-D each of which could connect nitrogen or the vacuum pump to the reaction vessel at S. Nitrogen was supplied from a cylinder and dried by passing through two drying tubes containing KOH and P_2O_5 before entering the apparatus. It was possible to connect other gases such as CO instead of nitrogen to the apparatus. A check on the passage of nitrogen could be confirmed by the bubbles at G. The vacuum line was connected to a pressure gauge and operated at around a pressure of 0.1 mm of Hg. Evaporated solvent was collected in a trap T cooled by liquid nitrogen at L. The techniques employed in using the apparatus are described in the following sections.

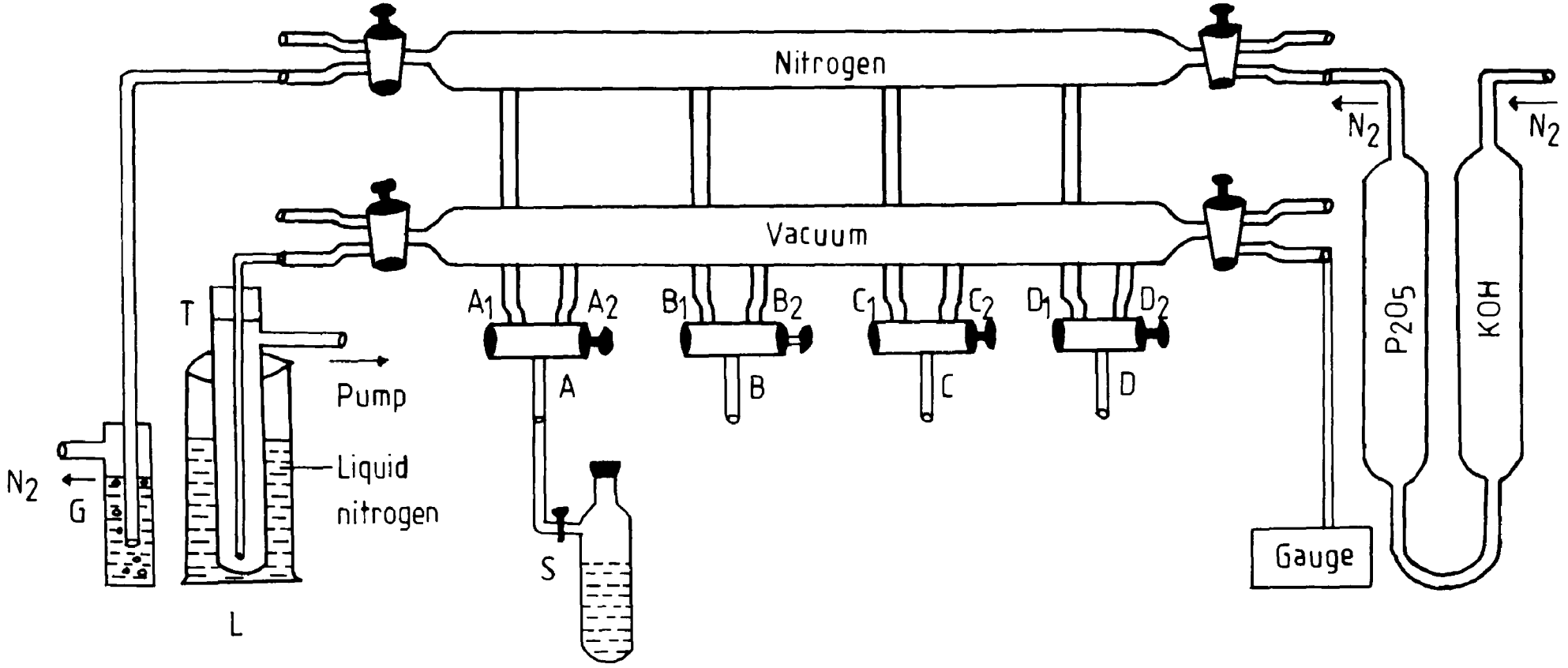


Figure 8 : Schlenk Apparatus

3.2. To De-gas Solvents

The solvent was placed in a Schlenk tube and the tube sealed with a Suba-seal. Tap S was then connected to the vacuum line at A and the tap A_2 was opened until bubbles appeared in the solution. This was done carefully in order that evaporation did not take place too vigourously. Both Taps S and A_2 were then closed and the system was opened to the nitrogen line at A_1. Tap S was opened until bubbles of nitrogen appeared at G. This procedure was then repeated three times after which the solvent could be considered to be degassed.

3.3. To Remove Solvent from the Reaction mixture

The tap of the Schlenk tube S was connected to the vacuum line at A_2 (A_1 closed). The solvent removed by the vacuum line as vapour was condensed in a trap T. During the removal of solvent the Schlenk tube was kept in a warm-water bath so that reaction mixture did not freeze. After evaporation of the solvent tap A_2 was closed and the whole system was pressurized with nitrogen.

3.4. Transferring solutions

One end of a metal, thin-bore transfer tube was inserted into the Schlenk tube 1 (from which solution was transferred). The other end of the transfer tube was

inserted into the Schlenk tube 2 (to which the solution was to be transferred). The system was evacuated and pressurized with nitrogen three times, before the end of the transfer tube was emerged into the solution in the Schlenk tube 1 as in figure 9.

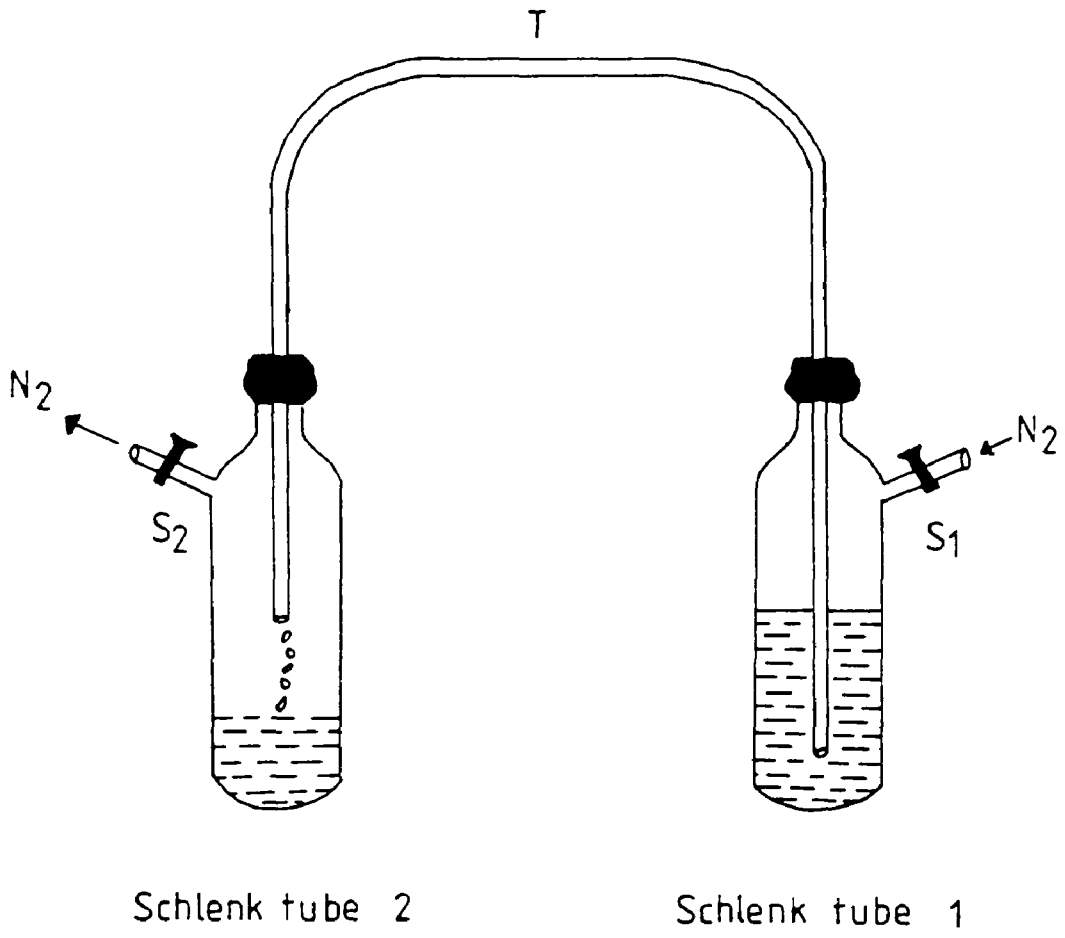


Figure 9 : Transferring a solution under nitrogen

Tap S_2 was opened to the vacuum line carefully at B. S_1 was closed. When all the solution was transferred S_2 was closed. Then S_2 was opened to nitrogen until the system was pressurized. The transfer tube was removed and the Schlenk tube 2 was sealed with a new Suba-seal under a positive pressure of N_2.

3.5. Reflux

A Schlenk tube containing degassed solvent and a magnetic stirrer was connected to the tap C through the top of the condenser. S was opened.

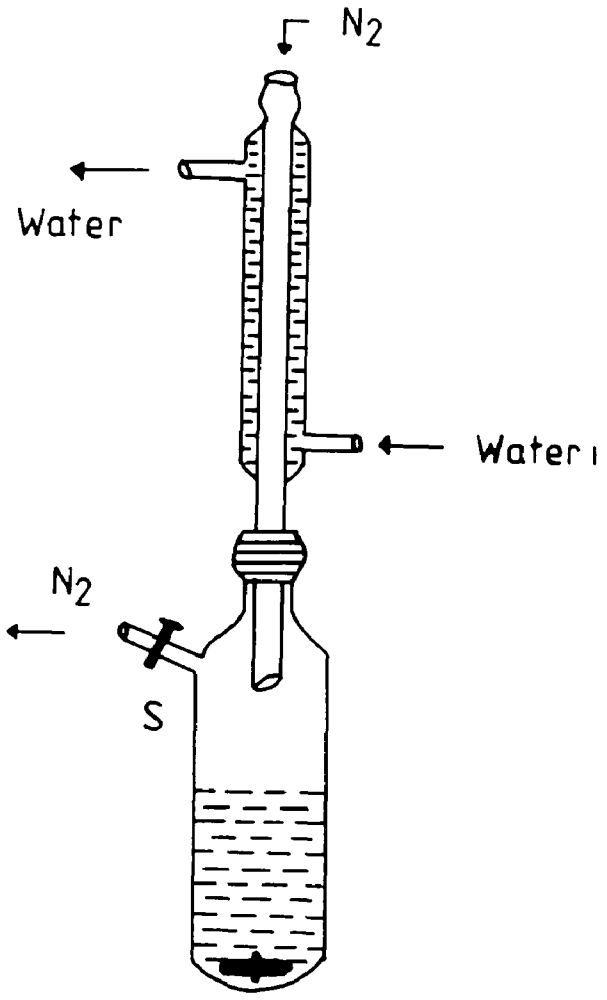


Figure 10 : Reflux under nitrogen

The whole system was flushed out with nitrogen admitting nitrogen at C and out at S for 10 minutes keeping taps S and C_1 opened (C_2 closed). The reactants were then added to the solvent under a positive nitrogen pressure

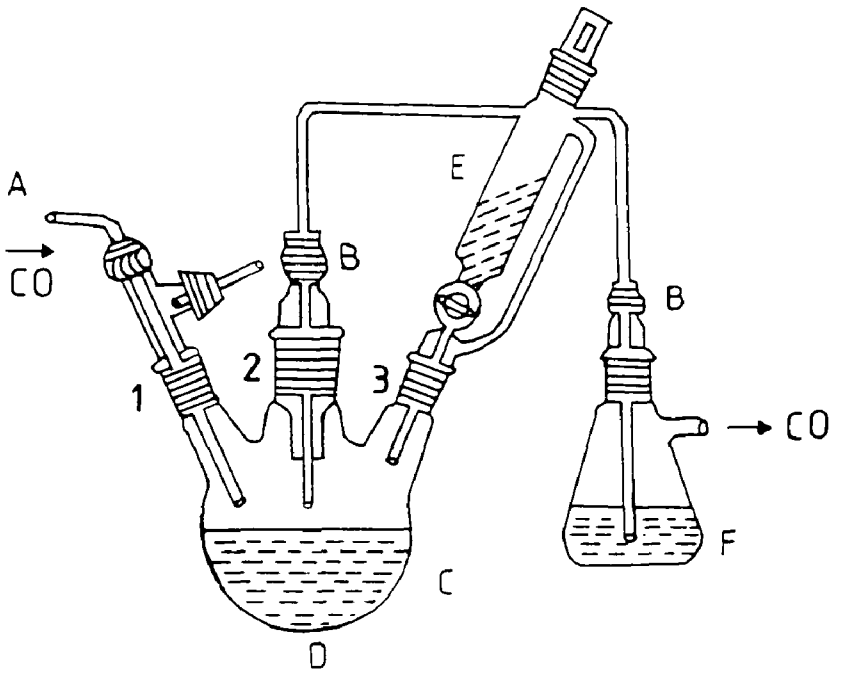
by removing the condenser slightly from the top of the Schlenk tube and admitting nitrogen at S.

3.6. Reactions Carried out under CO

Preparations involving CO were carried out in a three necked round bottomed flask (figure 11). A solution of the reagent to be reacted was placed in the flask together with a magnetic stirrer. The necks 1 and 2 were connected to CO inlet A and outlet B respectively so that CO could enter and leave the flask to pass through a trap containing paraffin oil. The neck 3 was attached to a dropping funnel. After flushing the apparatus with CO for five minutes, a solution of the other reactant was added via the dropping funnel.

3.7. Evans Method

The Evans method is used to determine whether a substance is paramagnetic or diamagnetic in solution. This method[82] involves the preparation of a solution of tetramethylsilane (TMS) in a deuterated solvent such as CD_2Cl_2 or $CDCl_3$ and comparison of the TMS ^{1}H-NMR proton resonance position with that of the same solution to which a known amount of the sample is added. The standard solution is placed in the inner compartment and the metal complex solution is placed in the outer



A = CO inlet

B = A cone joint in which a CO take off outlet is provided

C = Reaction solution

D = Magnetic stirrer

E = Dropping funnel

F = Paraffin oil

Figure 11 : Illustration of reaction flask equipped with magnetic stirrer, CO inlet and outlettubes and dropping funnel

compartment of a coaxial NMR tube. The magnetic susceptibility can then be calculated from the formula :

$$X_w = \frac{3\Delta\nu}{2\pi\nu c} + X_0 = X_m/M_r$$

where X_w = the mass susceptibility

X_m = the molar susceptibility

M_r = the relative molecular mass of the complex

X_0 = the mass susceptibility for the pure solvent (equal to -0.55×10^{-6} cm^3g^{-1} for CD_2Cl_2)

c = the concentration of the sample in g cm^{-3}

ν = the spectrometer frequency in hertz.

3.8. Instrumentation

(a). Electronic Spectra

Electronic spectra were measured on a Double Beam Computing CE 5500 Spectrophotometer, manufactured by CECIL Instruments Limited.

(b). Infrared Spectra

Infrared spectra (4000-600 cm^{-1}) were measured on a Perkin Elmer 881 Infrared Spectrophotometer and Perkin Elmer 681 Infrared Spectrophotometer. Far infrared spectra (600-250 cm^{-1}) were measured on Perkin Elmer 457 Infrared Spectrophotometer.

(c). Nuclear Magnetic Resonance Spectra

^{1}H and ^{31}P-NMR spectra were obtained using a JEOL FX 900 90 MHz Fourier Transform Spectrophotometer. ^{1}H-NMR spectra were recorded in $CDCl_3$ and acetone-d^6 solvents using TMS as an internal reference. ^{31}P-NMR (proton decoupled) spectra were recorded in CH_2Cl_2/D_2O and $CDCl_3$ using H_3PO_4 as an external reference. For air sensitive samples, nitrogen was bubbled through the sample solution in the NMR tube, then the tube sealed with a plastic cap.

(d). Magnetic Moments

Magnetic moments of solid samples were measured by a Johnson Matthey magnetic susceptibility balance. The balance was calibrated using $[HgCo(SCN)_4]$.

(e). Low Temperature Measurements

Low temperatures were measured by a Comark microprocessor thermometer made by Comark Electronics, Rustington, Sussex, England where Chromel-alumel wire was used.

3.9. Purification of Solvents

(a). Dichloromethane : The commercial grade of dichloromethane was purified by washing with 5% sodium

carbonate solution, followed by water, dried over anhydrous calcium chloride and finally distilled. The fraction at b.p. 40-41 ^{0}C was collected and stored over type 4A molecular sieves.

(b). Ethanol (Absolute alcohol) : A dry round bottomed flask (1.5-2.0 dm^3) was fitted with a double surface condenser and a calcium chloride guard tube. Clean dry magnesium turnings (5.0 gm) and iodine (5.0 g) were placed in the flask, followed by 75 cm^3 absolute alcohol. The mixture was warmed until the iodine colour (violet) had disappeared. Heating was continued until all the magnesium was converted to ethoxide , then 900 cm^3 absolute alcohol was added and the mixture was refluxed for 30 minutes. After cooling, the ethanol was distilled off directly into a vessel in which it was stored, by reassembling the condenser for downward distillation via a splash head adapter. Then the distilled ethanol was stored over type 4A molecular sieves.

(c). Methanol : Anhydrous methanol was obtained by distillation of methanol with magnesium turnings with exactly the same procedure as for ethanol.

(d). Benzene : Analytical grade benzene was first treated with anhydrous calcium chloride, filtered and then placed over sodium wire.

(e). Acetone : The acetone was heated under reflux with successive quantities of potassium permanganate until the violet colour persisted. It was then dried with anhydrous potassium carbonate, filtered from the dessicant and distilled. Precaution was taken to exclude moisture, i.e., a calcium chloride guard tube was used.

(f). Hexane : Analytical grade hexane was stored over type 4A molecular sieves.

(g). Tetrahydrofuran : Sodium wire and benzophenone were added to tetrahydrofuran until a blue colour persisted. Then the blue coloured solution was distilled under nitrogen and the fraction (b.p. 65-66 ^{0}C) was collected and stored over type 4A molecular sieves under nitrogen.

3.10. Chemicals

$Ph_2PCH_2PPh_2$ (dppm), $Ph_2PCH_2CH_2PPh_2$ (dppe), $NaBH_4$, $[Mo(CO)_3(C_7H_8)]$, $AgBF_4$, $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$, $[K_2(PdCl_4)]$ and $[K_2(PtCl_4)]$ were all obtained from the Aldrich Chemical Company. NiI_2, $Ni(NO_3)_2$ and $NiCl_2.6H_2O$ were obtained from BDH.

SECTION 4

REACTIVITY OF ZEROVALENT NICKEL-CO-PHOSPHINE COMPLEXES

4.1. INTRODUCTION

Transition metals do not form organometallic compounds in the same way as most other metals; instead their alkyl or aryl derivatives appear to be very unstable at room temperature[83]. The difference between transition metals and other metals[83] that the d orbitals in the valence shell of the transition metals have energy levels close to that of their valency s and p orbitals. This must account for the instability of their organic derivatives, because, electrons can easily be promoted from the relatively high energy filled d orbitals into antibonding σ^* orbitals of the metal-to-carbon orbitals, or, if the d orbitals are empty, from carbon-to-metal bonding orbitals into d orbitals, in either case weakening the metal-to-carbon bond. At any rate for the formation of stable organometallic compounds there should be more than a certain minimum difference energy (Δ E) (figure 12) between the highest energy-orbital which contain electrons and the lowest-energy orbitals which is vacant, but in most transition metal compounds this minimum is not attained.

Metals in the second half of the transition series e.g. Fe(II), Co(II), Ni(II), Cu(II) have occupied d orbitals which are not used in σ-bonding. These are the highest occupied energy levels in the complex and lower in energy than the antibonding σ^* levels. If the energy levels of the non-bonding occupied d orbitals of a metal

are lowered by combining them with π-type orbitals of low energy in suitable ligands, then the stability of the organo derivatives of that metal should be increased. Therefore, ligands capable of forming strong dative π bonds with the metal such as CO or phosphines i.e. strong field ligands, should increase the stability of alkyl or aryl derivatives of Ni(II). For this reason Ni(O)-CO-phosphine complexes would appear to be reasonable precursor compounds for the preparation of Ni(II) organo derivatives, via oxidative addition reactions with organic halides. It has already been reported[14] that the related Platinum complex $[Pt(CO)_2(phosphine)]$ (phosphine = PPh_3, d(*i*-Pr)pe) undergoes oxidative addition reactions with RX to form [PtXR(phosphine)] (R = Me, X = I).

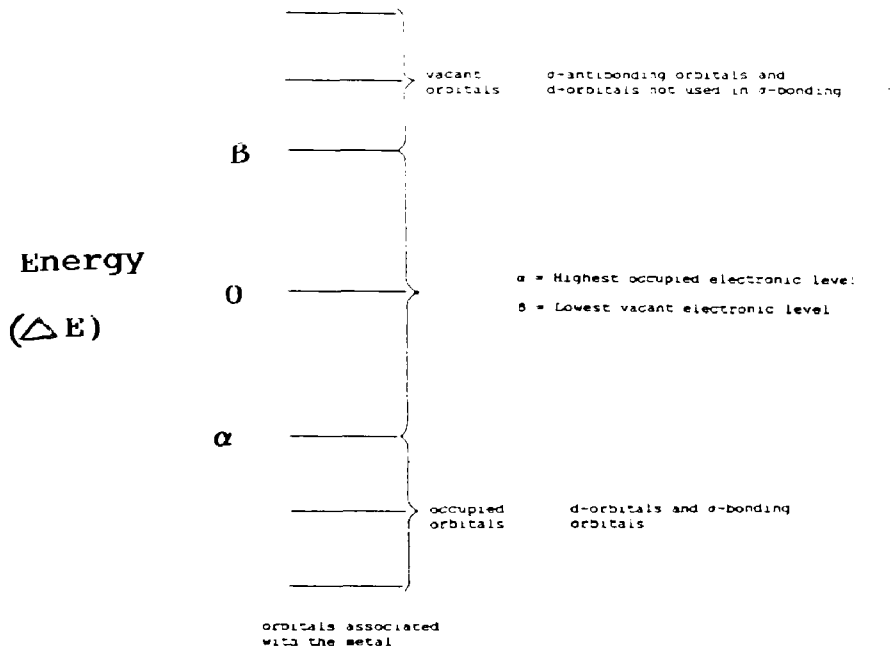


Figure 12 : Suggested condition for stability of organo-transition metal complexes

Also, Chatt and Shaw[84] have reported that the stability of organo-transition metal complexes with their d orbitals either occupied or used in σ bond formation will be greater when the ligands are in square planar or octahedral than when they are in tetrahedral configurations because the ligands in square and octahedral geometries form stronger dative π bonds than when they are in tetrahedral positions. Use of chelating/bridging diphosphines such as dppe, dppm in the precursor Ni(O) complexes may encourage square planar or octahedral geometries in the Ni(II) products since $[NiX_2(dppe\text{-}PP')]$ and $[NiX_2(dppm\text{-}PP')]$ tend to be square planar[85]. By analogy with the oxidative addition reactions of aryl halides with $[Ni(PPh_3)_4]$ [section 2.2.(a).(ii).] it might be expected that oxidative addition of organic halides to the complexes $[Ni(CO)(dppe\text{-}PP')(dppe\text{-}P)]$ and $[Ni(CO)_2(dppm\text{-}P)_2]$ could give organometallic oxidative products.

Reactions of acids or compound with activated hydrogen with zerovalent nickel complexes may result in the formation of stable Ni(II) hydride derivatives which may be used in the study of homogeneous hydrogenation and hydrogen transfer reactions. Therefore, the reactions of HCl gas with the zerovalent nickel complexes $[Ni(CO)(dppe\text{-}PP')(dppe\text{-}P)]$ and $[Ni(CO)_2(dppm\text{-}P)_2]$ have been investigated with the object of preparing Ni-H derivatives.

It has been reported[70-74] that zerovalent phosphine complexes of nickel, palladium and platinum react with molecular oxygen to give $[MO_2L_2]$ ($L = PPh_3$, M = Ni, Pd, Pt) and the phosphine oxide. Recently, D.G. Holah et al.[9] reported that the zerovalent nickel complex $[Ni_2(CO)_3(dppm\text{-}P)_3]$ is very reactive towards trace amounts of O_2 to give the monoxide of dppm. Therefore, the reactions of [Ni(CO)(dppe-PP')(dppe-P)] and $[Ni(CO)_2(dppm\text{-}P)_2]$ with air have been investigated in order to ascertain whether these complexes give products such as $[NiO_2L_2]$ (L_2 = dppe, dppm) or oxides of dppe and dppm. Investigation of these reactions also allowed possible identification of any impurities caused by any accidental oxidation of air sensitive Ni(O) species, when carrying out reactions using these species.

4.2. EXPERIMENTAL PROCEDURES

(a). Preparation[10] of [Ni(CO)(dppe-PP')(dppe-P)]

A suspension of 1,2-bis(diphenylphosphino)ethane (2.49 g, 6.25 mmol), in 10 cm^3 toluene, was stirred with CO passing through the suspension. A solution of hydrated nickel(II) chloride (0.50 g, 2.10 mmol) in 10 cm^3 ethanol was added dropwise to the mixture together with a suspension of sodium borohydride (0.24 g, 6.34 mmol) in 10 cm^3 ethanol. The colour of the reaction changed to yellow. The mixture was stirred under CO for 3 h. The resultant yellow precipitate was collected by filtration, washed with distilled water (10 cm^3 x 3), absolute alcohol (5 cm^3 x 3) and diethyl ether (5 cm^3 x 3), then dried in vacuo for 30 minutes. Yield : 1.65 g (90%).

IR (KBr disc) : $\tilde{\nu}$(CO) at 1911 (s) cm^{-1}, $\tilde{\nu}$(C-H) (aromatic) at 3050 (w), $\tilde{\nu}$(C-H) (aliphatic) at 2922 (w) cm^{-1}, $\tilde{\nu}$(P-Ph) at 1432 (s) cm^{-1}. The value for v(P-Ph) is in agreement with literature values[86,87].

^{31}P-NMR (CD_2Cl_2/H_3PO_4) : δ 43.5 (s), δ 30.9 (s), δ -13.0 (s). These values agree with reported values[10] for [Ni(CO)(dppe-PP')(dppe-P)].

(b). Preparation[10] of [Ni(CO)$_2$(dppm-P)$_2$]

To a solution of bis(diphenylphosphino)methane (2.4 g, 6.24 mmol) in warm toluene (13 cm^3), through which

carbon monoxide was passing, a solution of hydrated nickel(II) chloride (0.5 g, 2.10 mmol) in ethanol (5 cm^3) was added dropwise. A suspension of sodium borohydride (0.28 g, 7.40 mmol) in ethanol (8 cm^3) was then added and stirring was continued for 2 h. A white precipitate appeared which was collected by filtration, washed with water (10 cm^3 x 3), absolute alcohol (5 cm^3 x 3) and diethyl ether (5 cm^3 x 3) and dried in vacuo for 30 minutes. Yield : 1.30 g (40%).
IR (KBr disc) : $\tilde{\nu}$(CO) at 1986 (s), 1926 (s) cm^{-1}, $\tilde{\nu}$(C-H) (aromatic) at 3052 (w), $\tilde{\nu}$(C-H) (aliphatic) at 2999 (w) cm^{-1}, $\tilde{\nu}$(P-Ph) at 1431 (s) cm^{-1}. The $\tilde{\nu}$(CO) values[10] agree with literature values of $[Ni(CO)_2(dppm\text{-}P)_2]$.
^{31}P-NMR ($CDCl_3/H_3PO_4$) : δ 23.2 (s), δ -27.7 (s). These also agree with reported values[10].

(c). Reaction of [Ni(CO)(dppe-PP')(dppe-P)] with MeCOCl to Form $[NiCl_2(dppe\text{-}PP')]$

To a degassed solution of [Ni(CO)(dppe-PP')(dppe-P)] (0.20 g, 0.23 mmol) in dry dichloromethane (20 cm^3) a solution of acetyl chloride (0.09 g, 1.15 mmol) in the same solvent (5 cm^3) was added. Stirring was continued for 2-3 h under nitrogen at room temperature. The colour of the reaction mixture turned from yellow to orange. The reaction mixture was then filtered and diethyl ether added to the concentrated (5 cm^3) filtrate which gave an air stable orange coloured precipitate. The product was

collected by filtration, washed with diethyl ether (5 cm^3 x 3) and dried in vacuo. Yield : 0.09 g (80%).
IR (KBr disc) : $\tilde{\nu}$(CO) absent, $\tilde{\nu}$(P-Ph) at 1435 (s) cm^{-1}, $\tilde{\nu}$(C-H)(aromatic) at 3053 (w) cm^{-1} and $\tilde{\nu}$(C-H)(aliphatic) at 2911 (w) cm^{-1}. Far-IR (CsI disc) : $\tilde{\nu}$(Ni-Cl) at 328 (b) cm^{-1}, $\tilde{\nu}$(Ni-P) at 390 (b) cm^{-1}, agreeing with the literature values[85] for $\tilde{\nu}$(Ni-Cl) and $\tilde{\nu}$(Ni-P).
^{31}P-NMR ($CDCl_3/H_3PO_4$) : δ 57.1 (s).
The solid was found to be diamagnetic and also displayed this property in solution as measured by the Evans Method [section 3.7].

(d). Reaction of [Ni(CO)(dppe-PP')(dppe-P)] with Iodine : Synthesis of [NiI_2(dppe-PP')]

To a degassed solution of [Ni(CO)(dppe-PP')(dppe-P)] (0.14 g, 0.16 mmol) in dichloromethane (15 cm^3) a solution of iodine (0.04 g, 0.16 mmol) in the same solvent (5 cm^3) was added dropwise under nitrogen. The mixture was stirred for 4 h under nitrogen at room temperature. The reaction mixture was filtered, the filtrate concentrated to approximately 5 cm^3, then diethyl ether added. Purple coloured crystals were obtained. The product was separated by filtration, washed by diethyl ether (5 cm^3 x 3) and then dried in vacuo. Yield : 0.09 g (80%).
IR (KBr disc) : $\tilde{\nu}$(CO) absent. $\tilde{\nu}$(C-H) (aromatic) at 3053 (w) cm^{-1}, $\tilde{\nu}$(C-H) (aliphatic) at 2942 (w) cm^{-1}, $\tilde{\nu}$(P-Ph) at 1433 (s) cm^{-1}.

^{31}P-NMR ($CDCl_3/H_3PO_4$) : δ 77.5 (s). The solid was found to be diamagnetic.

(e). Reaction of [Ni(CO)(dppe-PP')(dppe-P)] with PhCOCl : Formation of a mixture of [$NiCl_2$(dppe-PP')] and [Ni(dppe-PP')$_2$]

[Ni(CO)(dppe-PP')(dppe-P)] (0.20 g, 0.23 mmol) was placed in dry degassed dichloromethane (15 cm^3) and stirred under nitrogen. A solution of benzoyl chloride (0.16 g, 1.14 mmol) in the same solvent (5 cm^3) was added to the solution and the reaction mixture was stirred for 4 h at room temperature. An orange precipitate was collected by the addition of diethyl ether to the concentrated filtrate (5 cm^3). The precipitate was filtered off and then washed with diethyl ether (5 cm^3 x 3) and dried in vacuo. The product was found to be a mixture of two compounds, [$NiCl_2$(dppe-PP')] and [Ni(dppe-PP')$_2$].

IR (KBr disc) : ν(C-H) (aromatic) at 3053 (w), ν(C-H) (aliphatic) at 2942 (w) cm^{-1}, ν(P-Ph) at 1435 (s) cm^{-1}.

Far-IR (CsI) : ν(Ni-Cl) (terminal) at 328 (b) cm^{-1}, ν(Ni-P) at 390 cm^{-1}(b).

^{31}P-NMR ($CDCl_3/H_3PO_4$) : δ 57.1 (s), δ 32.9 (s).

(f). Reaction of [Ni(CO)(dppe-PP')(dppe-P)] with Alkyl and Aryl Halides : Attempts to Synthesize Ni-Alkyl and Ni-Aryl Complexes

[Ni(CO)(dppe-PP')(dppe-P)] was reacted with several alkyl and aryl halides i.e. methyl iodide, ethyl iodide, cyclohexyl bromide, bromobenzene and chlorobenzene in dichloromethane. The halides were added in a five fold molar excess. Stirring was continued for 12 h at room temperature. A light yellow coloured crude product was collected in each of the reactions which on reprecipitation from a dichloromethane/diethyl ether mixture gave an off-white coloured product.

IR (KBr disc) : $\tilde{\nu}$(CO) absent. $\tilde{\nu}$(C-H) (aromatic) and (aliphatic) at 3052 (w) and 2941 (w) cm^{-1} respectively, $\tilde{\nu}$(P-Ph) at 1438 (s) cm^{-1}.

^{31}P-NMR ($CDCl_3/H_3PO_4$) : around δ 32.0 (s) in each case.

(g). Reaction of $[Ni(CO)_2(dppm\text{-}P)_2]$ with Iodine : Synthesis of a mixture of $[NiI_2(dppm\text{-}PP')]$ and $[NiI_2(dppm\text{-}P)_2]$

To a degassed solution of $[Ni(CO)_2(dppm\text{-}P)_2]$ (0.20 g, 0.22 mmol) in dichloromethane (15 cm^3), a solution of iodine (0.08 g, 0.31 mmol) in the same solvent (5 cm^3) was added dropwise under nitrogen. The reaction mixture was stirred for 4 h. The reaction mixture was filtered and concentrated to approximately 5 cm^3. Upon addition of diethyl ether, a purple coloured precipitate formed.

The product was separated by filtration, washed with diethyl ether (5 cm^3 x 3) and dried in vacuo.

IR (KBr disc) : $\tilde{\nu}$(CO) absent, $\tilde{\nu}$(C-H) (aromatic) at 3053 (w), $\tilde{\nu}$(C-H) (aliphatic) at 2919 (w) cm^{-1}, $\tilde{\nu}$(P-Ph) at 1434 (s) cm-1.

^{31}P-NMR ($CDCl_3/H_3PO_4$) : δ 33.6 (s), δ 27.0 (s), δ 23.8 (s), δ -32.5 (s).

(h). Reaction of [Ni(CO)(dppe-PP')(dppe-P)] with HCl gas : Formation of a mixture of a Nickel Hydride Complex and [$NiCl_2$(dppe-PP')]

[Ni(CO)(dppe-PP')(dppe-P)] (0.62 g, 0.70 mmol) was placed in a 250 cm^3 round bottomed flask with 50 cm^3 of toluene. Sublimed aluminium trichloride (0.094 g, 0.67 mmol) was added. The mixture was degassed and HCl gas was condensed into the flask. The mixture was then stirred at room temperature for 20 h and the resultant orange precipitate was collected by filtration and washing with diethyl ether (5 cm^3 x 3). The product found was a mixture of a nickel hydride and [$NiCl_2$(dppe-PP')].

IR (KBr disc): $\tilde{\nu}$(CO) absent. A broad band in the region 3600-2600 cm^{-1}.

^{1}H-NMR ($CDCl_3$) : Ni-H at δ -13.04. This value is in agreement with a literature value[76] of Ni-H of $[NiH(dppe\text{-}PP')_2]^+$.

^{31}P-NMR ($CDCl_3/H_3PO_4$) : δ 44.5 (s), δ 57.1 (s).

(i). Reaction of [Ni(CO)(dppe-PP')(dppe-P)] with Air : Formation of $[Ni(dppe\text{-}PP')_2]$

Dichloromethane (30 cm^3) was taken in a small beaker. (0.22 g, 0.25 mmol) [Ni(CO)(dppe-PP')(dppe-P)] was dissolved in the solvent and the yellow coloured solution was allowed to stand in air for a week at room temperature. Removal of the solvent gave a pale green precipitate which was dried in vacuo. Part of this product dissolved in $CDCl_3$ and the solution was subjected to ^{31}P-NMR.

IR (KBr disc) : $\tilde{\nu}$(CO) absent. No $\tilde{\nu}$(P=O) or $\tilde{\nu}$(O-O) were observed.

^{31}P-NMR ($CDCl_3/H_3PO_4$) : δ 32.6 (s).

(j). Reaction of $[Ni(CO)_2(dppm\text{-}P)_2]$ with Air : Formation of a mixture of $[Ph_2P(O)CH_2PPh_2]$ and $[Ph_2P(O)CH_2P(O)Ph_2]$

$[Ni(CO)_2(dppm\text{-}P)_2]$ (0.22 g, 0.25 mmol) was dissolved in dichloromethane (20 cm^3). The solution was left in air for a week. Removal of solvent gave a pale green coloured product. Part of this product dissolved in $CDCl_3$, the solution was subjected to ^{31}P-NMR.

IR (KBr disc) : $\tilde{\nu}$(CO) absent. $\tilde{\nu}$(P=O) observed at 1215 (s) cm^{-1}. This value agrees with the literature[88]. No $\tilde{\nu}$(O-O) was observed.

^{31}P-NMR ($CDCl_3/H_3PO_4$) : δ 28.9 (d, ^2J(P-P) 50 Hz), δ -28.4 (d, ^2J(P-P) 50 Hz), δ 24.6 (s). The first two values agree with literature values[89] of

$[Ph_2P(O)CH_2PPh_2]$. δ 24.6 (s) also agrees with literature value[89] of $[Ph_2P(O)CH_2P(O)Ph_2]$.

(k). Reaction[90] of dppe with Air : Formation of $[Ph_2P(O)(CH_2)_2P(O)Ph_2]$

1,2-bis(diphenylphosphino)ethane (1.0 g, 2.51 mmol) was dissolved in ethanol and hydrogen peroxide (30 wt.%) was added. The mixture was exposed to air for a week. Colourless crystals of the product were obtained, which were filtered, washed with ethanol (5 cm^3 x 2) followed by diethyl ether (5 cm^3 x 3) and then dried in vacuo. Yield : 0.74 g (70%).
IR (KBr disc) : $\bar{\nu}$(C-H) (aromatic) at 3053 (w), $\bar{\nu}$(C-H) (aliphatic) at 2924 (w) cm^{-1}, $\bar{\nu}$(P-Ph) at 1435 (s) cm^{-1}. $\bar{\nu}$(P=O) at 1197 (s) cm^{-1}.
^{31}P-NMR ($CDCl_3$) : δ 35.0 (s).

4.3. Literature Preparations

The following compounds were prepared using literature methods and their ^{31}P-NMR spectra obtained. This was done with the purpose of identifying the products of the reactions in [section 4.2.]. The ^{31}P-NMR values are previously unreported. The complexes prepared are given with their ^{31}P-NMR values in the following table :

Complex	Reference for prep.	^{31}P-NMR Spectra (ppm)
$[NiCl_2(dppe\text{-}PP')]$	82	57.6 (s)
$[NiCl_2(dppm\text{-}P)_2]$	91	32.7 (b), -29.4 (b)
$[NiI_2(dppe\text{-}PP')_2]$	92	48.6 (s)
$[NiI_2(dppm\text{-}PP')]$	93	26.1 (s), 33.5 (s)
$[NiI_2(dppm\text{-}P)_2]$	91	-31.5 (s)
$[Ni_2I_2(\mu\text{-}I)_2(dppm\text{-}PP')_2]$	93	20.2 (s)
$[Ni(dppe\text{-}PP')_2]$	94	32.4 (s)

4.4. RESULTS AND DISCUSSION

(a). Nickel(0)-Carbon monoxide-Phosphine Complexes [Ni(CO)(dppe-PP')(dppe-P)] and [$Ni(CO)_2(dppm\text{-}P)_2$]

The starting materials, [Ni(CO)(dppe-PP')(dppe-P)] and [$Ni(CO)_2(dppm\text{-}P)_2$] have been prepared [section 4.2.(a). and (b).] using literature procedures[10], except that toluene was used as solvent instead of benzene.

The infrared spectrum of [Ni(CO)(dppe-PP')(dppe-P)] (KBr disc) (figure 13) exhibits a $\tilde{\nu}$(CO) stretching frequency at 1911 (s) cm^{-1}.

The ^{31}P-NMR spectrum of tetrahedral [Ni(CO)(dppe-PP')(dppe-P)] (figure 14) gives three singlet resonances found at δ 43.5 (s), δ 30.9 (s) and δ -13.0 (s)[10] which are assigned for two equivalent phosphorus atoms of dppe ligand bonded to nickel in a chelate fashion, one phosphorus atom of monodentate dppe bonded to nickel and free phosphorus atom of the same ligand respectively. These values are in agreement with the literature values[10] of [Ni(CO)(dppe-PP')(dppe-P)].

The infrared spectrum of the complex [$Ni(CO)_2(dppm\text{-}P)_2$] (KBr disc) (figure 15) gives $\tilde{\nu}$(CO) at 1986 (s) and 1926 (s) cm^{-1} which agree with the reported $\tilde{\nu}$(CO) values[10] for [$Ni(CO)_2(dppm\text{-}P)_2$].

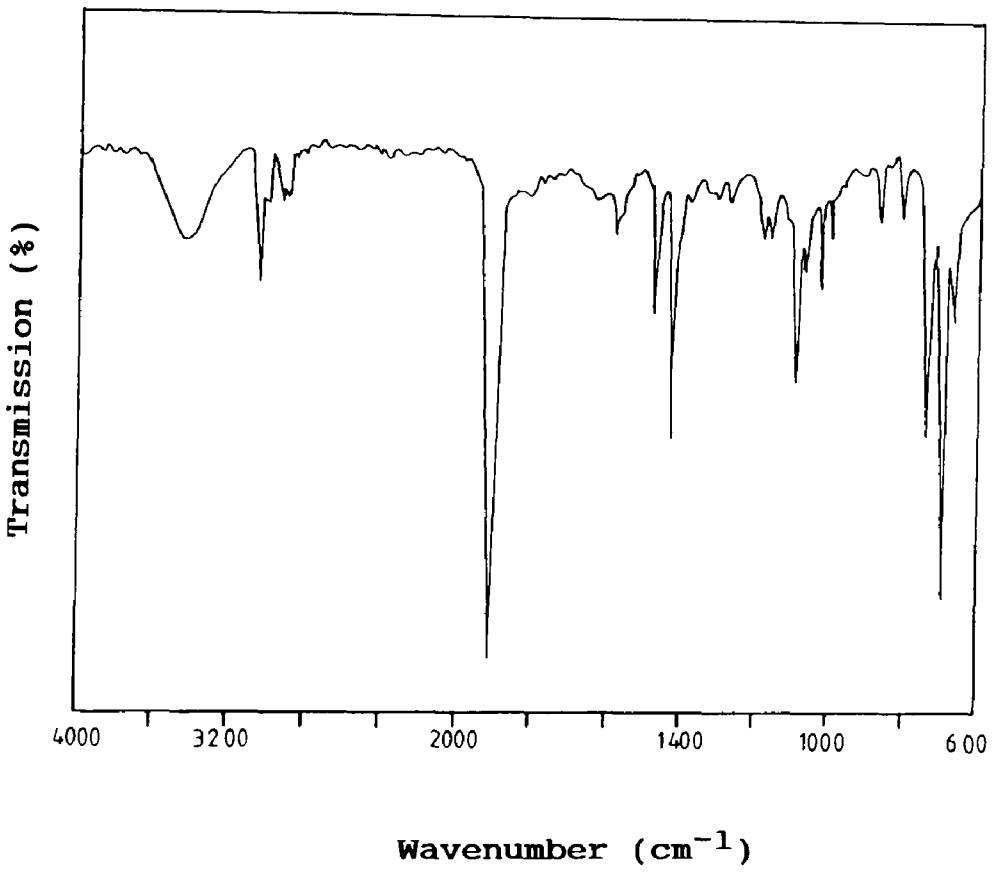


Figure 13 : IR spectrum of [Ni(CO)(dppe-PP')(dppe-P)] (in KBr disc)

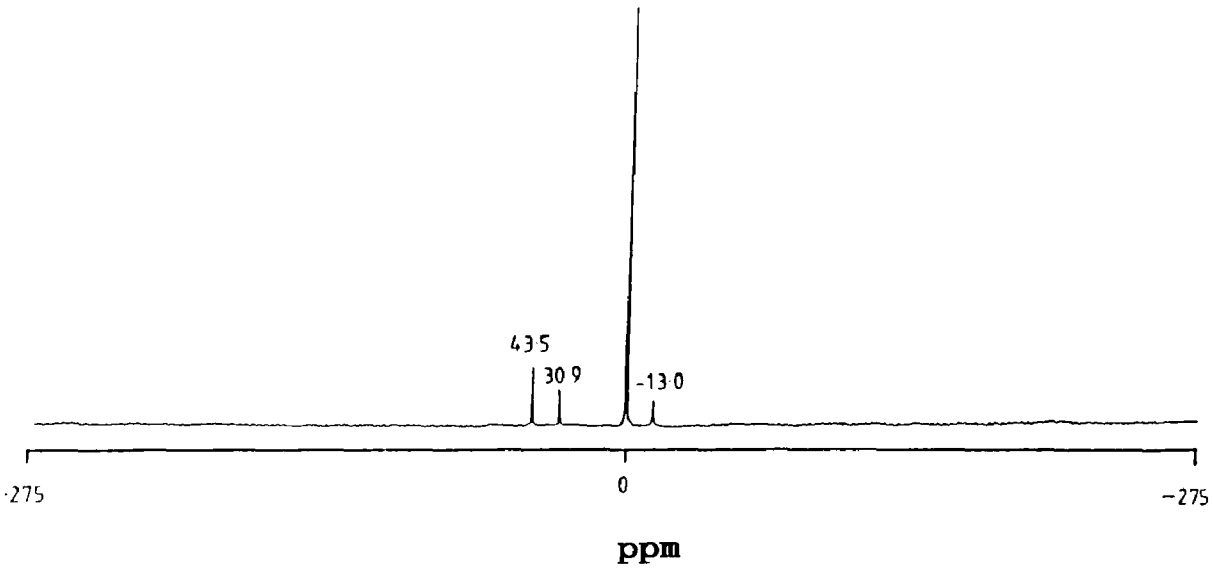


Figure 14 : ^{31}P-NMR spectrum of [Ni(CO)(dppePP')(dppe-P)] (in $CDCl_3$, 85% H_3PO_4)

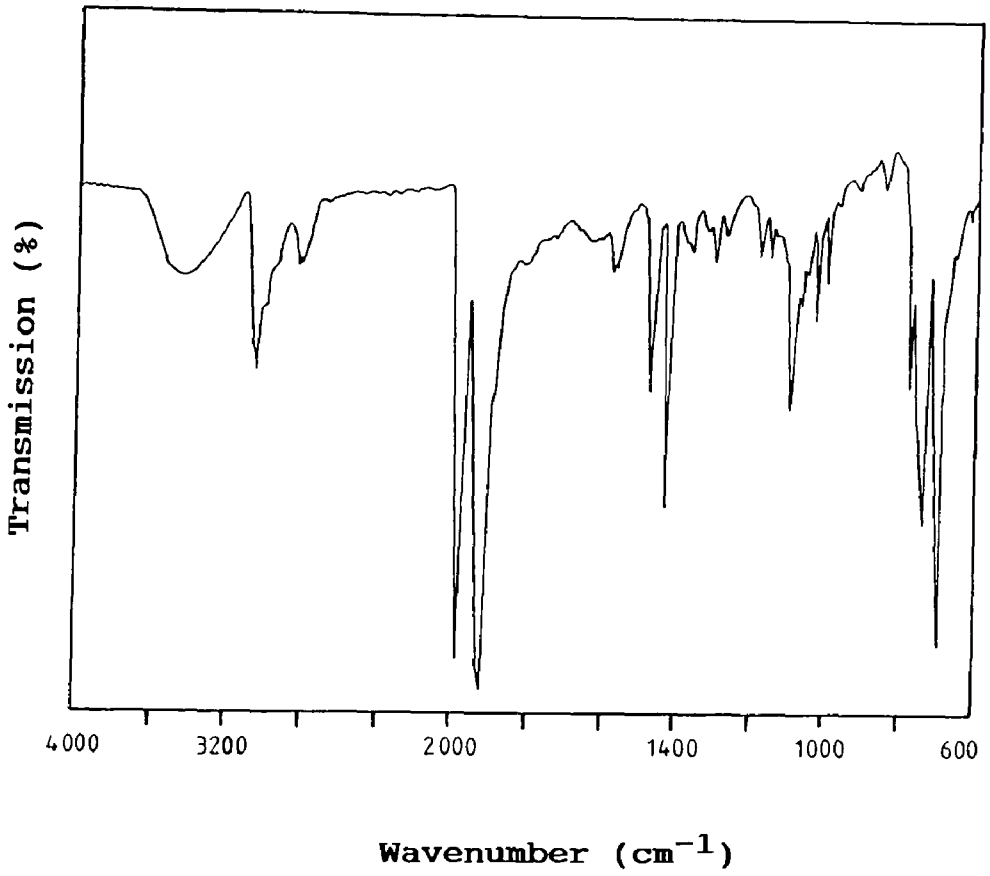


Figure 15 : IR spectrum of $[Ni(CO)_2(dppm\text{-}P)_2]$ (in KBr disc)

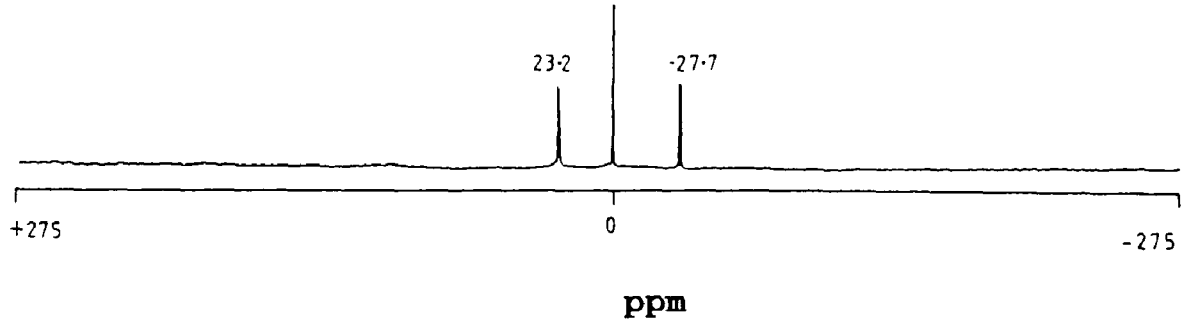


Figure 16 : ^{31}P-NMR spectrum of $[Ni(CO)_2(dppm\text{-}P)_2]$ (in $CDCl_3$, 85% H_3PO_4)

The ^{31}P-NMR spectrum of tetrahedral $[Ni(CO)_2(dppm\text{-}P)_2]$ (figure 16) consists of two singlet resonances at δ 23.2 and δ -27.7 which are assigned for the phosphorus atoms bonded to nickel and the free phosphorus atoms of monodentate dppm ligands[10] of $[Ni(CO)_2(dppm\text{-}P)_2]$ respectively.

(b). Reaction of [Ni(CO)(dppe-PP')(dppe-P)] with MeCOCl : Synthesis of $[NiCl_2(dppe\text{-}PP')]$

The reaction of [Ni(CO)(dppe-PP')(dppe-P)] with MeCOCl [section 4.2.(c).] produced simply a bis chloro Ni(II) complex, $[NiCl_2(dppe\text{-}PP')]$ instead of a Ni-acyl organometallic complex.

Magnetic moment measurements showed that the product is diamagnetic both in solid and solution indicating square planar geometry; this is in agreement with the literature findings[95] for the same substance. The product gave a positive Lassaigne fusion test for chlorine.

The infrared spectrum of the product (KBr disc) (figure 18) does not show any ν(CO) in the carbonyl region. The bands observed at 3053 (w) and 2911 (w) cm^{-1} have been assigned for the aromatic ν(C-H) and aliphatic ν(C-H) stretching bands respectively. The spectrum also exhibits a sharp absorption band at 1435 (s) cm^{-1} which indicates[86,87] ν(P-Ph). The far infrared spectrum of the

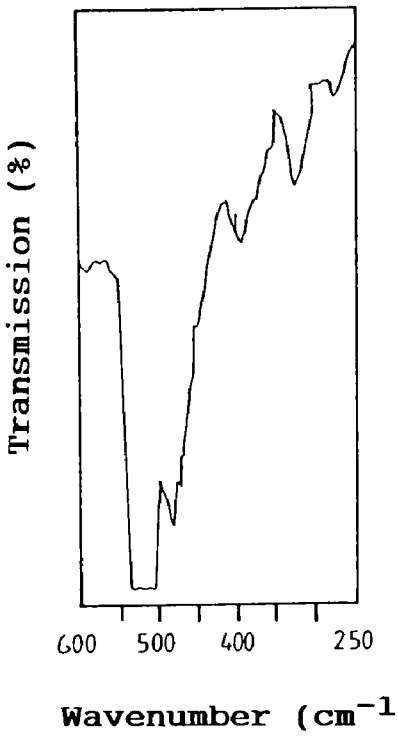


Figure 17 : Far IR spectrum of [$NiCl_2$(dppe-PP')] (in CsI disc)

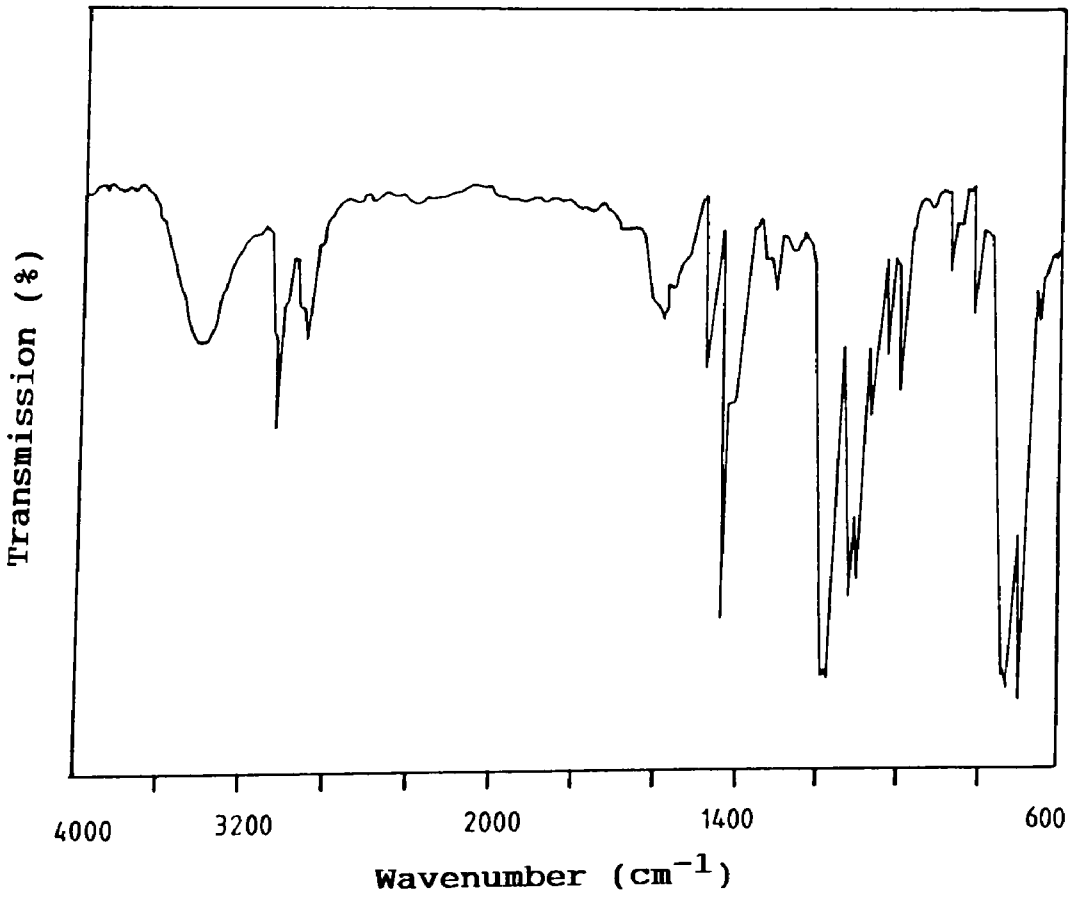


Figure 18 : IR spectrum of [$NiCl_2$(dppe-PP')] (in KBr disc)

complex (CsI disc) (figure 17) exhibits a broad band at 328 cm^{-1} which is due to the terminal[85] ν(Ni-Cl) and a band at 390 cm^{-1} which is assigned[85] to ν(Ni-P). *Cis* square planar nickel-halogen phosphine complexes give two values for ν(Ni-Cl); the symmetric and anti-symmetric stretch bands. M. Hidai et al.[12] and Boorman and Carty[85] have reported that ν(Ni-Cl) for [$NiCl_2$(dppe-PP')] are at 330 and 320 cm^{-1}. The *cis* complex is expected to give two bands at lower frequency[85] (in the range 313-330 cm^{-1}) than ν(Ni-Cl) for the trans complex[85] (in the range 407-403 cm^{-1}) owing to the higher trans effect of phosphine. Therefore, the broad band found at 328 cm^{-1} is proposed as representing two bands for ν(Ni-Cl) which overlap with each other. The far IR spectrum of a sample [$NiCl_2$(dppe-PP')] produced by the literature procedure[82] gives a broad band for ν(Ni-Cl) at 329 cm^{-1} (appendix figure 1).

The ^{31}P-NMR spectrum of the product (figure 19) exhibits a singlet signal at δ 57.1 which has been assigned for two equivalent phosphorus atoms of the dppe ligand bonded to nickel in a chelating fashion. This value compares with that one of the complex [$NiCl_2$(dppe-PP')] prepared directly from $NiCl_2.6H_2O$ and dppe ligand using a known procedure[82] which gave a singlet at δ 57.6 in its ^{31}P-NMR spectrum (appendix figure 2).

Therefore, the solid product of the reaction has been

identified as $[NiCl_2(dppe\text{-}PP')]$. The structure of this complex is given in figure 5.

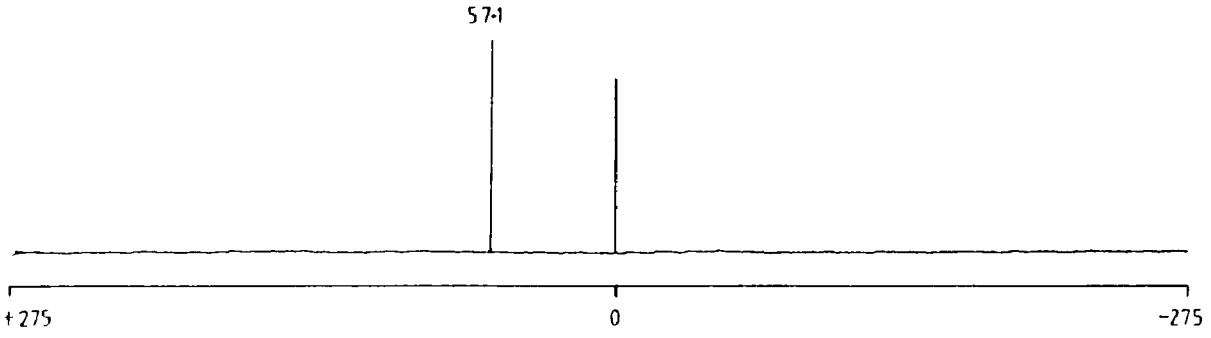


Figure 19 : ^{31}P-NMR spectrum of $[NiCl_2(dppe\text{-}PP')]$ (in $CDCl_3$, 85% H_3PO_4)

(c). Reaction of $[Ni(CO)(dppe\text{-}PP')(dppe\text{-}P)]$ with Iodine : Formation of $[NiI_2(dppe\text{-}PP')]$

The reaction of iodine with $[Ni(CO)(dppe\text{-}PP')(dppe\text{-}P)]$ [section 4.2.(d).] gave a violet coloured product which was characterized as $[NiI_2(dppe\text{-}PP')]$.

The infrared spectrum of the product (KBr disc) (figure 20) shows no $\tilde{\nu}(CO)$ in the carbonyl region. It also shows bands at 3053 (w), 2942 (w) and 1433 (s) cm^{-1} which are due to aromatic $\tilde{\nu}(C\text{-}H)$, aliphatic $\tilde{\nu}(C\text{-}H)$ and $\tilde{\nu}(P\text{-}Ph)$[86,87] respectively. The far infrared spectrum of the complex (CsI disc) did not show a band for $\tilde{\nu}(Ni\text{-}I)$. Values for $\tilde{\nu}(Ni\text{-}I)$ generally appear[82,96] below 250 cm^{-1} and available instrumentation did not cover this region.

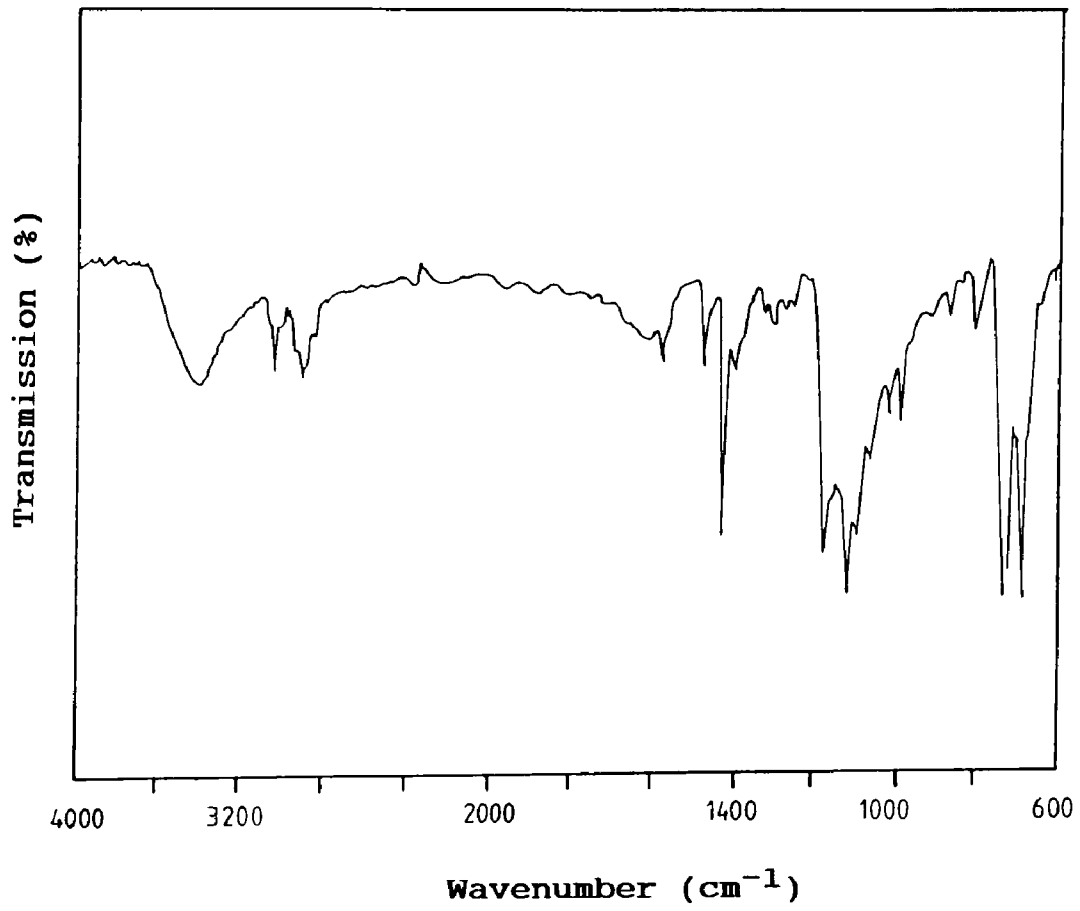


Figure 20 : IR spectrum of [NiI_2(dppe-PP')] (in KBr disc)

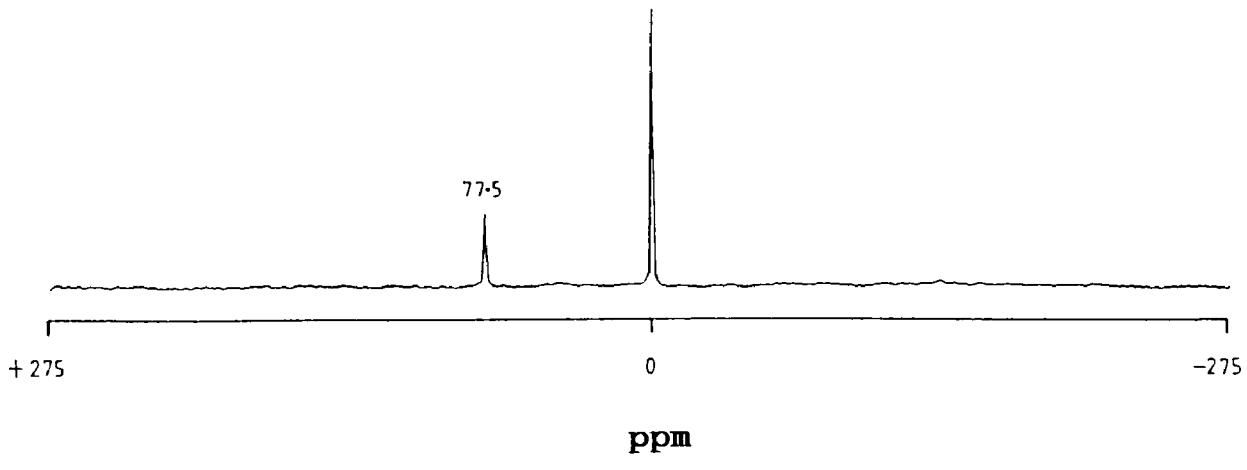


Figure 21 : ^{31}P-NMR spectrum of [NiI_2(dppe-PP')] (in $CDCl_3$, 85% H_3PO_4)

A Lassaigne fusion test showed a positive test for iodine. Magnetic susceptibility measurements of the product indicated that it was diamagnetic, again indicating square planar geometry.

The ^{31}P-NMR spectrum of the product (figure 21) consists of a singlet at δ 77.5. Attempts to prepare [NiI_2(dppe-PP')] were carried out using the general preparation of bis halo Ni(II) phosphine complexes of the type[82,92,97-98] [NiX_2(dppe-PP')](X = Cl, Br and I). However, a yellow coloured product was formed whose ^{31}P-NMR spectrum gave a singlet at δ 48.5, as well as a very small resonance at δ 77.4. The octahedral complex, [NiI_2(dppe-PP')$_2$] was prepared by following a known procedure reported by G. Booth et al.[92] and formed as a yellow product, the ^{31}P-NMR of which gave a singlet at δ 48.6 (appendix figure 3). M. J. Hudson et al.[98] reported that recrystallization of [NiI_2(dppe-PP')$_2$] formed [NiI_2(dppe-PP')]. [NiI_2(dppe-PP')$_2$] was[92,98] recrystallized from ethyl alcohol and [NiI_2(dppe-PP')] was partially formed. The ^{31}P-NMR spectrum of the recrystallized product showed two singlets at δ 77.2 and δ 48.5 (appendix figure 4). Since the latter is known for the complex [NiI_2(dppe-PP')$_2$], it is concluded that the singlet observed at δ 77.2 is due to the phosphorus atoms of the dppe ligand in [NiI_2(dppe-PP')].

Therefore, it is concluded that the reaction of iodine with [Ni(CO)(dppe-PP')(dppe-P)] gives the *cis* square

planar diamagnetic complex, $[NiI_2(dppe\text{-}PP')]$, the structure of which is suggested as in figure 22.

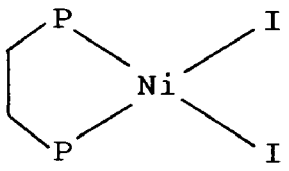


Figure 22 : Structure of $[NiI_2(dppe\text{-}PP')]$

(d). Reaction of $[Ni(CO)(dppe\text{-}PP')(dppe\text{-}P)]$ with PhCOCl : Formation of a mixture of $NiCl_2(dppe\text{-}PP')]$ and $[Ni(dppe\text{-}PP')_2]$

Addition of PhCOCl to $[Ni(CO)(dppe\text{-}PP')(dppe\text{-}P)]$ gave an orange coloured product [section 4.2.(e)] which has been characterized as a mixture of $[NiCl_2(dppe\text{-}PP')]$ and $[Ni(dppe\text{-}PP')_2]$.

The infrared spectrum of the mixture formed (KBr disc) (figure 24) exhibits no $\bar{\nu}(CO)$ in the carbonyl region. The far infrared spectrum of the mixture (CsI disc) (figure 23) gives a broad band at 328 cm^{-1} which has been assigned to the terminal[85] $\bar{\nu}(Ni\text{-}Cl)$'s of $[NiCl_2(dppe\text{-}PP')]$, [section 4.4.(b).]. The far infrared also shows a band at 390 cm^{-1} assigned[85] to $\bar{\nu}(Ni\text{-}P)$ of $[NiCl_2(dppe\text{-}PP')]$. A Lassaigne fusion test of the mixture showed the presence of chlorine.

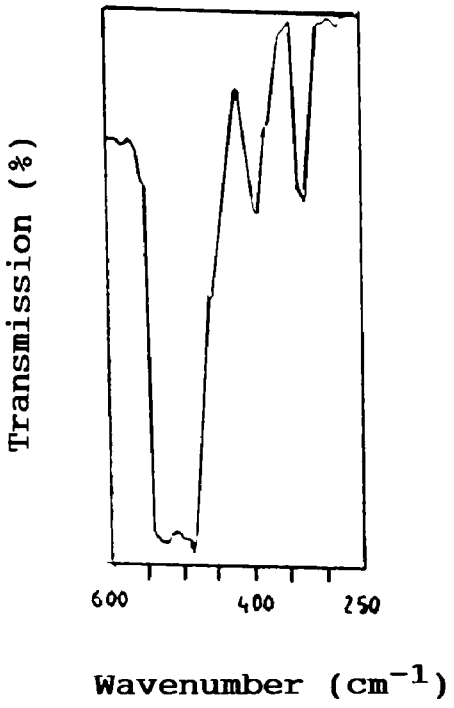


Figure 23 : Far IR spectrum of the product of reaction 4.4.(b). (In CsI disc)

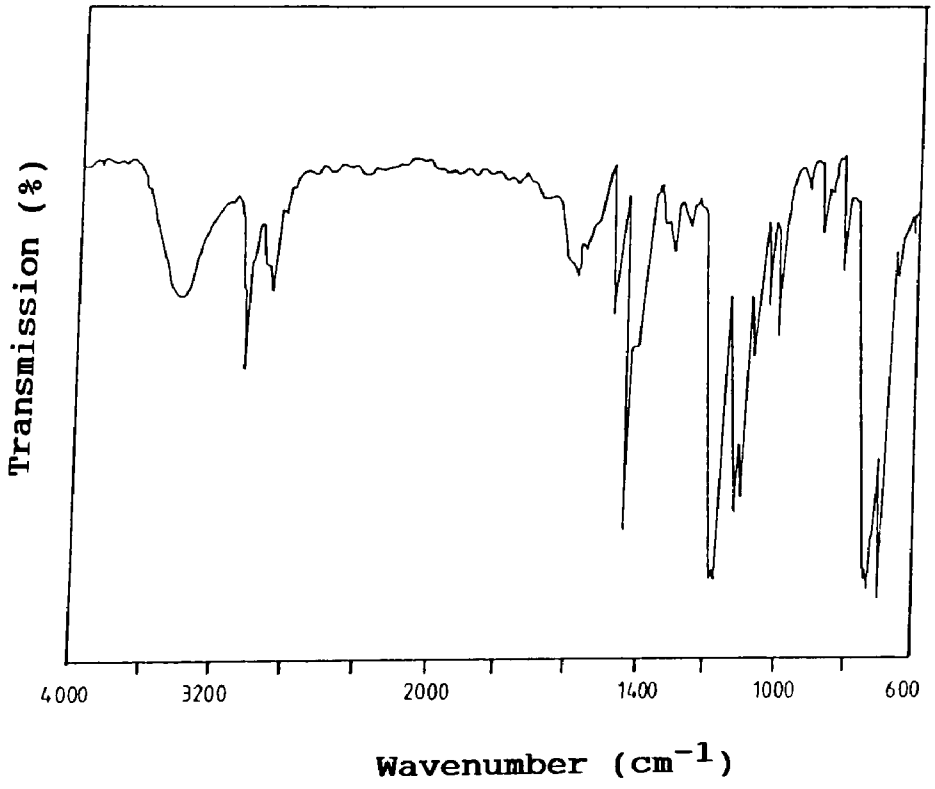


Figure 24 : IR spectrum of the product of reaction 4.4.(b) (in KBr disc)

The ^{31}P-NMR spectrum of the mixture (figure 25) shows two singlet signals at δ 57.1 and δ 32.9. The resonance found here at δ 57.1 has already been characterized for the two equivalent phosphorus atoms of $[NiCl_2(dppe\text{-}PP')]$ [section 4.4.(b).]. L. Malatesta et al.[69] showed that the reaction of zerovalent metal-phosphine complexes with alkyl, aryl or aroyl halides could give, depending on the reaction conditions the bis halo derivatives, MX_2L_2. Therefore, this result is in agreement with their findings. The resonance found at δ 32.9 is suggested as representing $[Ni(dppe\text{-}PP')_2]$. This was prepared by the reduction[94] of $[NiBr_2(dppe\text{-}PP')_2]$ by $NaBH_4$ [section 4.3]. The ^{31}P-NMR of the complex showed a singlet at δ 32.4 (appendix figure 5) representing four equivalent phosphorus atoms.

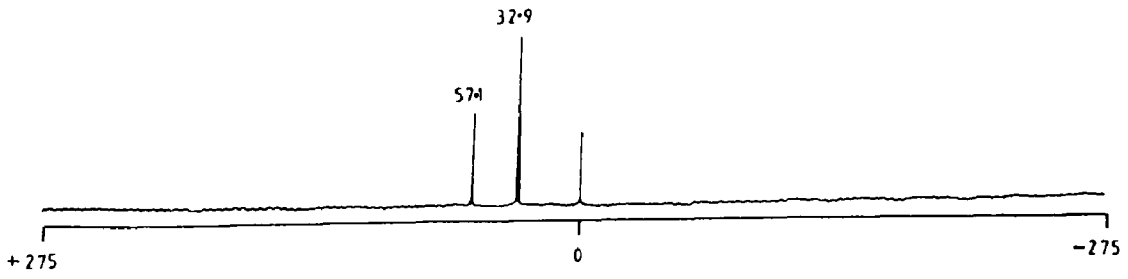


Figure 25 : ^{31}P-NMR spectrum of product of reaction 4.4.(d). (in $CDCl_3$, 85% H_3PO_4)

It is therefore proposed that the products of this reaction are $[NiCl_2(dppe\text{-}PP')]$ and $[Ni(dppe\text{-}PP')_2]$. The

aroyl product if formed, decomposes to give $[NiCl_2(dppe\text{-}PP')]$ and $[Ni(dppe\text{-}PP')_2]$ (figure 26).

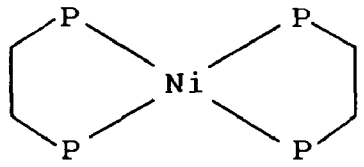


Figure 26 : Structure of $[Ni(dppe\text{-}PP')_2]$

(e). Reaction of $[Ni(CO)(dppe\text{-}PP')(dppe\text{-}P)]$ with Alkyl and Aryl Halides : Formation of $[Ni(dppe\text{-}PP')_2]$

The reactions of $[Ni(CO)(dppe\text{-}PP')(dppe\text{-}P)]$ with alkyl and aryl halides e.g., methyl iodide, ethyl iodide, cyclohexyl bromide, chlorobenzene and bromobenzene respectively gave yellow crude products in each case, the infrared of which (KBr disc) exhibited two strong $\tilde{\nu}(CO)$ stretching frequencies at or near 1995 and 1934 cm^{-1}. These two values are consistent with that of[37] $[Ni(CO)_2(dppe\text{-}PP')]$ (appendix table 1). Reprecipitation of these products from a dichloromethane/diethyl ether mixture gave an off-white coloured product the infrared spectra of which (KBr disc) did not show bands for $\tilde{\nu}(CO)$. The infrared spectra also showed bands at 3052 (w), 2941 (w) and 1438 (s) cm^{-1} assigned for $\tilde{\nu}(C\text{-}H)$ (aromatic), $\tilde{\nu}(C\text{-}H)$ (aliphatic) and $\tilde{\nu}(P\text{-}Ph)$[86,87].

The ^{31}P-NMR of these products (figure 27) all showed a singlet absorbance at around δ 32.0 which has been

assigned to the phosphorus atoms of [Ni(dppe-PP')$_2$] [section 4.4.(d)].

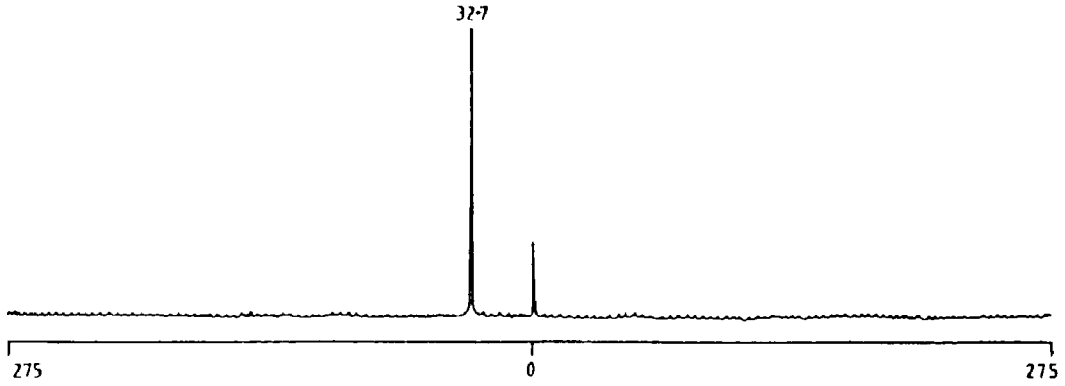


Figure 27 : ^{31}P-NMR spectrum of [Ni(dppe-PP')$_2$] from the reaction of [Ni(CO)(dppe-PP')(dppe-P)] with methyl iodide (in $CDCl_3$, 85% H_3PO_4).

(f). Reaction of [Ni(CO)$_2$(dppm-P)$_2$]) with Iodine : Formation of a mixture of [NiI$_2$(dppm-PP')] and [NiI$_2$(dppm-P)$_2$]

The reaction of iodine with [Ni(CO)$_2$(dppm-P)$_2$] produces a mixture of the diiodo Ni(II) products, [NiI$_2$(dppm-PP')] and [NiI$_2$(dppm-P)$_2$] which have been characterized from IR, ^{31}P-NMR spectra and UV/visible spectra.

The infrared spectrum of the mixture (KBr disc) (figure 28) shows no $\tilde{\nu}$(CO) in the carbonyl region. It gives $\tilde{\nu}$(C-H) (aromatic) and $\tilde{\nu}$(C-H) (aliphatic) at 3053 (w) and 2919 (w) cm^{-1} respectively. It also gives an absorption

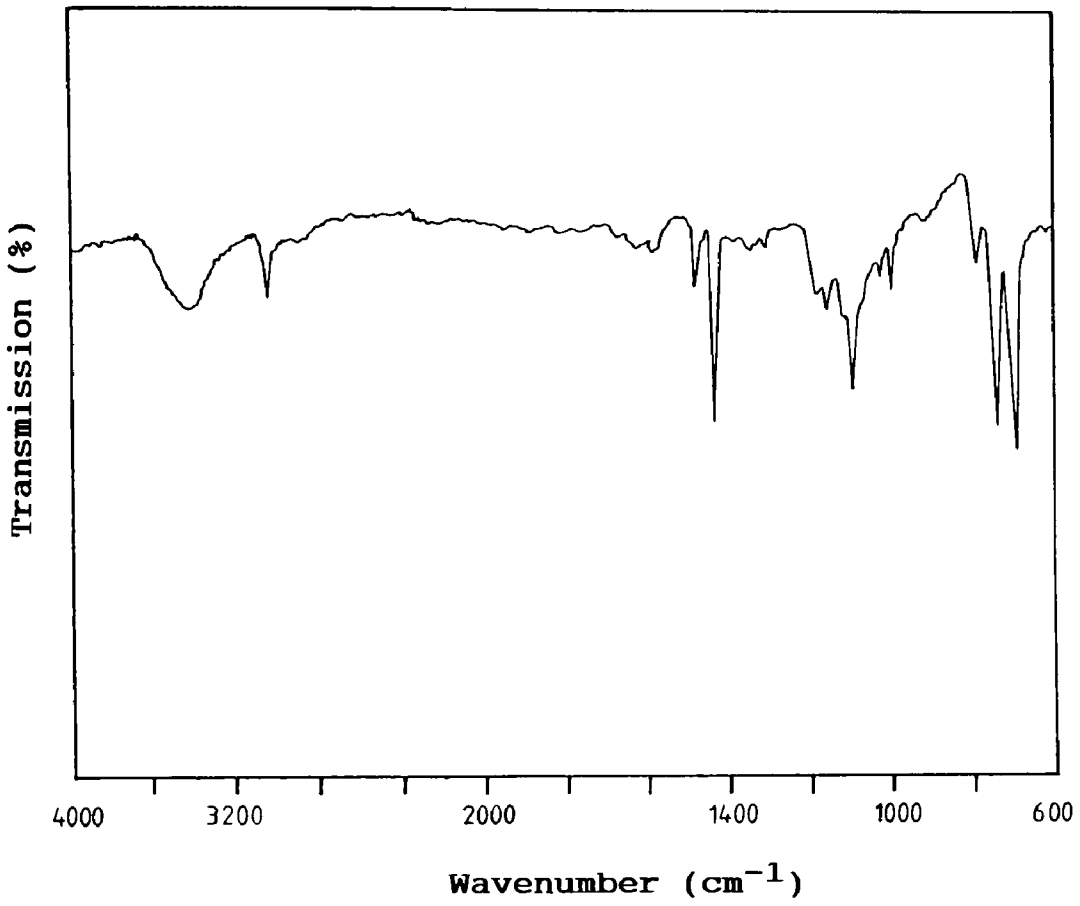


Figure 28 : IR spectrum of product of reaction 4.4.(f). (in KBr disc)

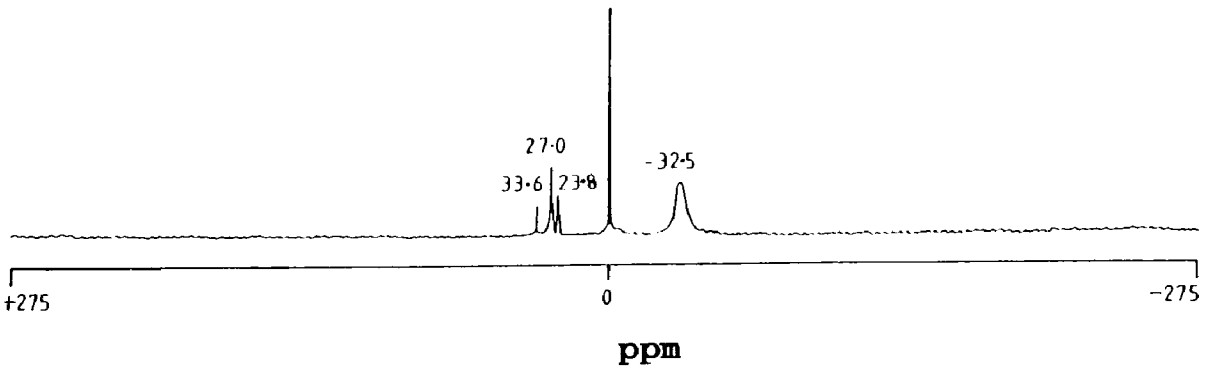


Figure 29 : ^{31}P-NMR spectrum of product of reaction 4.4.(f). (in $CDCl_3$, 85% H_3PO_4)

band at 1434 (s) cm^{-1} for $\tilde{\nu}$(P-Ph)[86,87]. The far infrared spectrum of the product shows a broad band in the region 540-510 cm^{-1}. C. Ercolani et al.[93] have mentioned that a band at 540-535 cm^{-1} is characteristic of chelating dppm. The far infrared spectra of free dppm and $[NiI_2(dppm\text{-}P)_2]$ show no bands in this region. Therefore, the broad band found at 540-510 cm^{-1} may be suggested for chelating dppm of $[NiI_2(dppm\text{-}PP')]$. A Lassaigne fusion test of the mixture gave a positive test for iodine.

The ^{31}P-NMR spectra of the product (Figure 29) shows a broad resonance at δ -32.5 and three singlets at δ 33.6, 27.0 and 23.8 respectively. The ^{31}P-NMR of the starting material $[Ni(CO)_2(dppm\text{-}P)_2]$ shows two singlet resonances at δ 23.2 and δ -27.7. So the resonance found at δ 23.8 may be due to the starting material[10] or another decomposition product. A broad resonance at δ -32.5 may due to $[NiI_2(dppm\text{-}P)_2]$. $[NiI_2(dppm\text{-}P)_2]$ has been prepared directly [section 4.3.] as purple mycrocrystals by following a known literature procedure[91]. The ^{31}P-NMR spectrum of this at room temperature shows a broad singlet resonance at δ -31.5 (appendix figure 7). Both free and coordinated phosphorus are present in $[NiI_2(dppm\text{-}P)_2]$ but it gives only a singlet resonance. The possibility is, there may be a very fast rate of exchange between the coordinated and free phosphorus atoms of $[NiI_2(dppm\text{-}P)_2]$ in solution and therefore it gives an broader average resonance in its ^{31}P-NMR

spectrum. This type of behaviour[99] has been observed in a mixture of nickel phosphine complex $[Ni(CN)_2\{P(OEt)_3\}_3]$ and free $P(OEt)_3$. This result was the same at -50 ^{0}C. A species in which dppm acts as a chelating ligand, $[NiI_2(dppm\text{-}PP')]$, have been prepared from NiI_2 and dppm by using a known literature procedure[93] [section 4.3.]. The ^{31}P-NMR spectrum of the product (appendix figure 6) gives two singlet resonances at δ 33.5 and 26.1 which indicates a mixture of two components. Therefore, comparison of these spectral values with those found for the mixture formed by the reaction of $[Ni(CO)_2(dppm\text{-}P)_2]$ with iodine suggests that the broad resonance observed at δ -32.5 can be suggested for[91] $[NiI_2(dppm\text{-}P)_2]$ (figure 29) and either δ 33.6 (s) or 27.0 (s) could be assigned for $[NiI_2(dppm\text{-}PP')]$ (figure 29). C. Ercolani et al.[93] have reported that recrystallization of $[NiI_2(dppm\text{-}PP')]$ sometimes results in the formation of $[NiI_2(dppm\text{-}P)_2]$ and an iodo bridged dimer $[Ni_2I_2(\mu\text{-}I)_2(dppm\text{-}PP')_2]$. The authors have also mentioned that $[Ni_2I_2(\mu\text{-}I)_2(dppm\text{-}PP')_2]$ reverts slowly to $[NiI_2(dppm\text{-}PP')]$ when dissolved in dichloromethane. This suggests that the three iodo complexes of nickel are interconvertable. Diamagnetic low spin 5-coordinate distorted square pyramidal $[Ni_2I_2(\mu\text{-}I)_2(dppm\text{-}PP')_2]$ has been prepared[93] as olive green powder from the reflux reaction of $[NiCl_2(dppm\text{-}PP')]$ with 20% MeI [section 4.3.]. The ^{31}P-NMR spectrum gives a very sharp singlet at δ 20.2, together with weak signals from species presumed to be impurities. Therefore, it can be

suggested that the reaction of $[Ni(CO)_2(dppm\text{-}P)_2]$ with iodine may produce $[NiI_2(dppm\text{-}PP')]$ with a mixture of $[NiI_2(dppm\text{-}P)_2]$, although no $[Ni_2I_2(\mu\text{-}I)_2(dppm\text{-}PP')_2]$ appears to be present in solution.

The UV/visible spectrum of $[NiI_2(dppm\text{-}PP')]$ has already been reported[93] where an absorbance is found at 540 nm for d-d electron transition. The UV/visible spectrum of the product formed in this reaction is shown in figure 30. An absorbance is found at 529 nm which may be considered[93] for d-d electron transition of $[NiI_2(dppm\text{-}PP')]$.

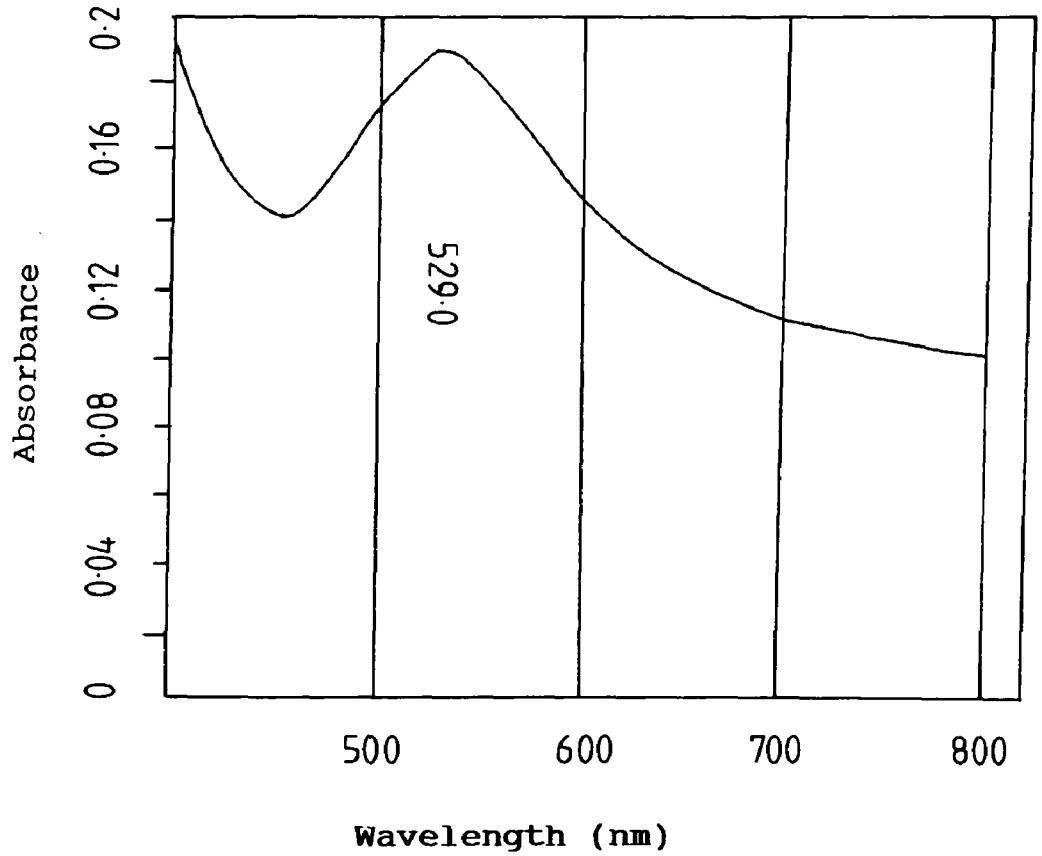


Figure 30 : UV/visible spectrum of product of reaction 4.4.f. (dissolved in dichloromethane).

This value of absorbance has been compared to that of $[NiI_2(dppm\text{-}PP')]$ produced from the literature synthesis[93], where the absorbance is recorded at 533 nm for d-d electron transition. Again, literature reports[91,93] show that both $[NiI_2(dppm\text{-}PP')]$ and $[NiI_2(dppm\text{-}P)_2]$ absorb at around 530-540 nm to give d-d electron transition. Therefore, the absorbance found at 529 nm may be considered for d-d electronic transition of a mixture of these two complexes, but not for $[Ni_2I_2(\mu\text{-}I)_2(dppm\text{-}PP')_2]$ because it absorbs at ca. 750 nm to give d-d electron transition . These results again suggest that the product may contain $[NiI_2(dppm\text{-}PP')]$ and/or $[NiI_2(dppm\text{-}P)_2]$ but not $[Ni_2I_2(\mu\text{-}I)_2(dppm\text{-}PP')_2]$.

Therefore, on the basis of evidences found from UV/visible, IR and ^{31}P-NMR spectra it can be suggested that addition of iodine to $[Ni(CO)_2(dppm\text{-}P)_2]$ produces a mixture of the four coordinate diamagnetic, square planar Ni(II) monomeric complexes $[NiI_2(dppm\text{-}PP')]$ and $[NiI_2(dppm\text{-}P)_2]$. The structures of these complexes are as follows in figure 31.

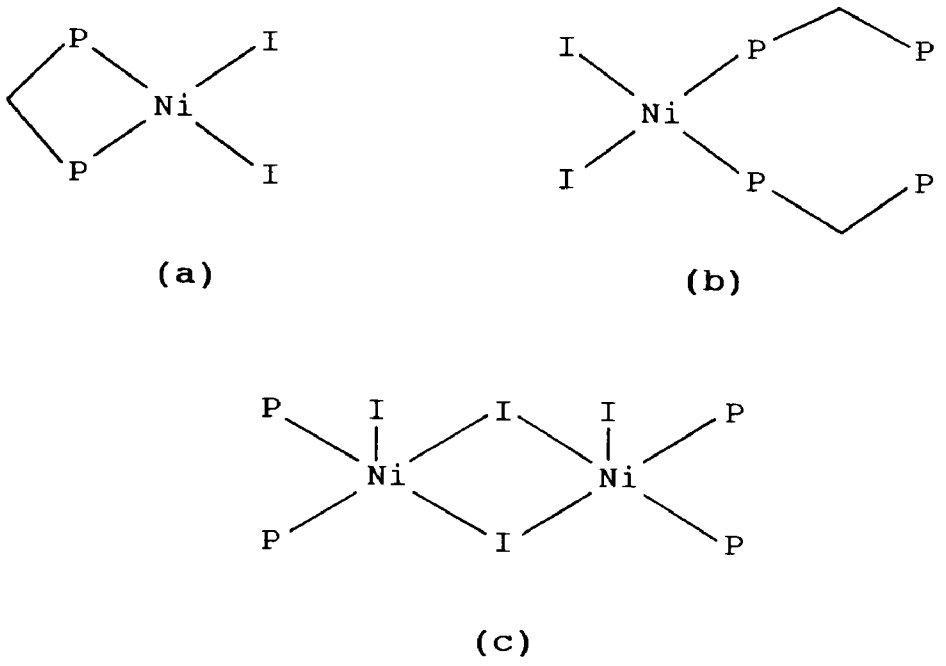


Figure 31 : Structures of (a). $[NiI_2(dppm\text{-}PP')]$ (b). $[NiI_2(dppm\text{-}P)_2]$ (c). $[Ni_2I_2(\mu\text{-}I)_2(dppm\text{-}PP')_2]$

(g). Reaction of Ni(CO)(dppe-PP')(dppe-P)] with HCl gas : Formation of a mixture of a Nickel Hydride Complex and $[NiCl_2(dppe\text{-}PP')]$

The addition of HCl gas to a solution of complex [Ni(CO)(dppe-PP')(dppe-P)] [section 4.2.(h).] produces a mixture of a stable nickel hydride complex, possibly $[NiH(dppe\text{-}PP')_2]^+X^-$ (X = $AlCl_4^-$) and $[NiCl_2(dppe\text{-}PP')]$.

The infrared spectrum of the product (KBr disc) (figure 32) shows a weak absorption band at 1911 cm^{-1} which is in the region reported for ν(Ni-H)[76]. However, the band may be due to the ν(CO) of unreacted [Ni(CO)(dppe-PP')(dppe-P)], because this shows ν(CO) at 1911 cm^{-1}. The spectrum also shows a broad band in the region 3600-2600 cm^{-1} probably from water which may be

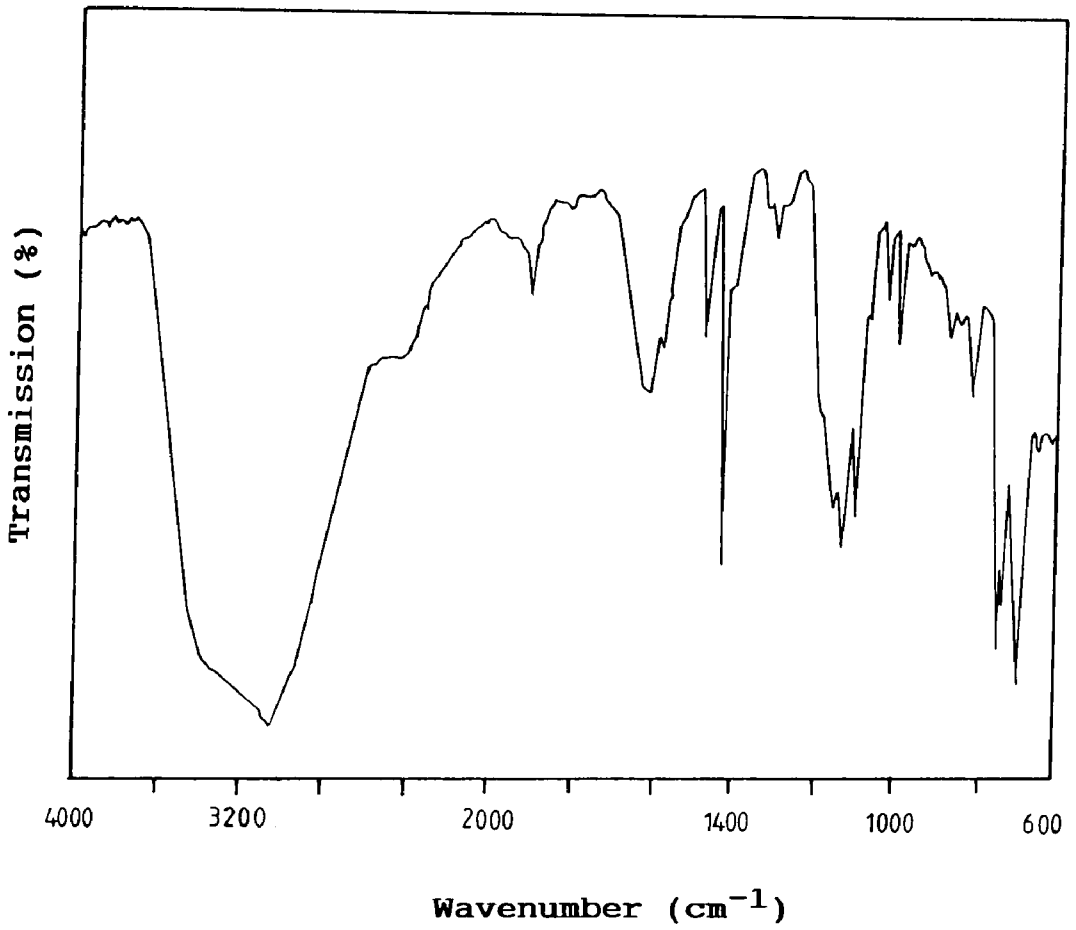


Figure 32 : IR spectrum of product of reaction 4.4.(g). (in KBr disc)

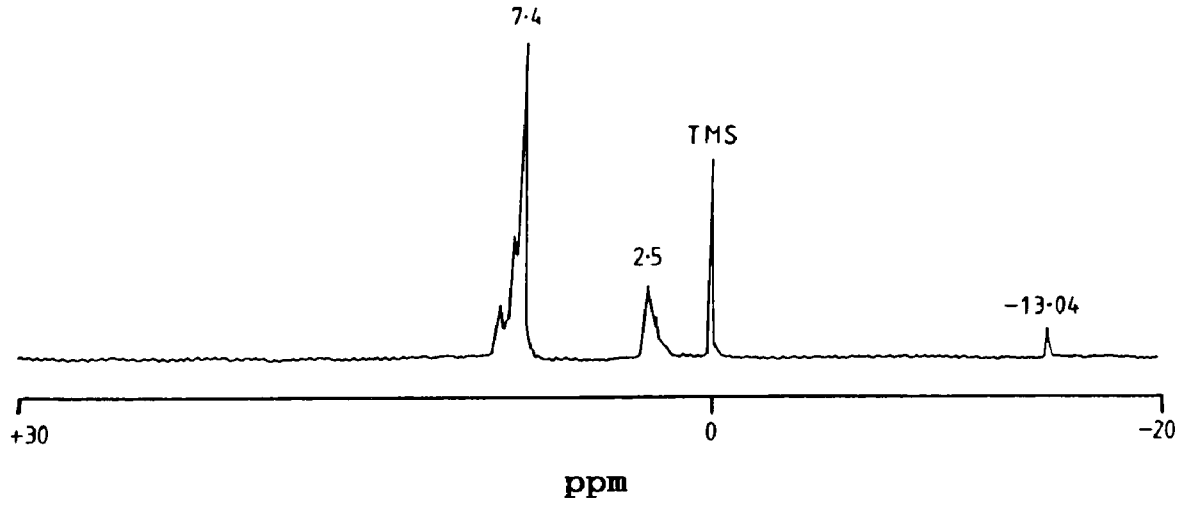


Figure 33 : High field ^{1}H-NMR spectrum of product of reaction 4.4.(g). (in $CDCl_3$, TMS)

absorbed by HCl gas during the time of reaction. The far infrared spectrum of the product (CsI disc) gives a broad band in the region 510-400 cm^{-1}. The far infrared region would be expected to contain $\bar{\nu}$(Al-Cl) which has been reported[100] in the region 650-350 cm^{-1}, bands for dppe (free dppe gives three sharp bands at 505, 475 and 438 cm^{-1}), therefore $\bar{\nu}$(Al-Cl) can not be definitely identified in this spectrum.

The high field ^{1}H-NMR spectrum of the product (figure 33) exhibits a broad resonance signal in the metal hydride region at δ -13.04 which has been assigned for nickel bonded hydrogen[76] i,e, Ni-H. The position of this resonance is characteristic of and diagnostic for a proton directly bonded to a transition metal[101]. The value δ -13.04 is consistent with the literature value of the resonance of the proton[76] in $[NiH(dppe\text{-}PP')_2]^+AlCl_4^-$. It has been reported that $[NiH(dppe\text{-}PP')_2]^+AlCl_4^-$ shows an unresolved Ni-H resonance[76] at δ -13.07 in CD_2Cl_2 but a resolved quintet at δ 13.00 only in MeOH with coupling constant, J(P-H) = 6 Hz. In the spectrum in figure 33, a broad unresolved Ni-H resonance has been found for which J(P-H) can not be measured.

The ^{31}P-NMR spectrum of the product (figure 34) gives two singlet resonances at δ 44.5 and 57.1. The Ni(II) complex $[NiCl_2(dppe\text{-}PP')]$ already characterized

[section 4.4.(b).] gives a singlet resonance at δ 57.1 in its ^{31}P-NMR spectrum (figure 19).

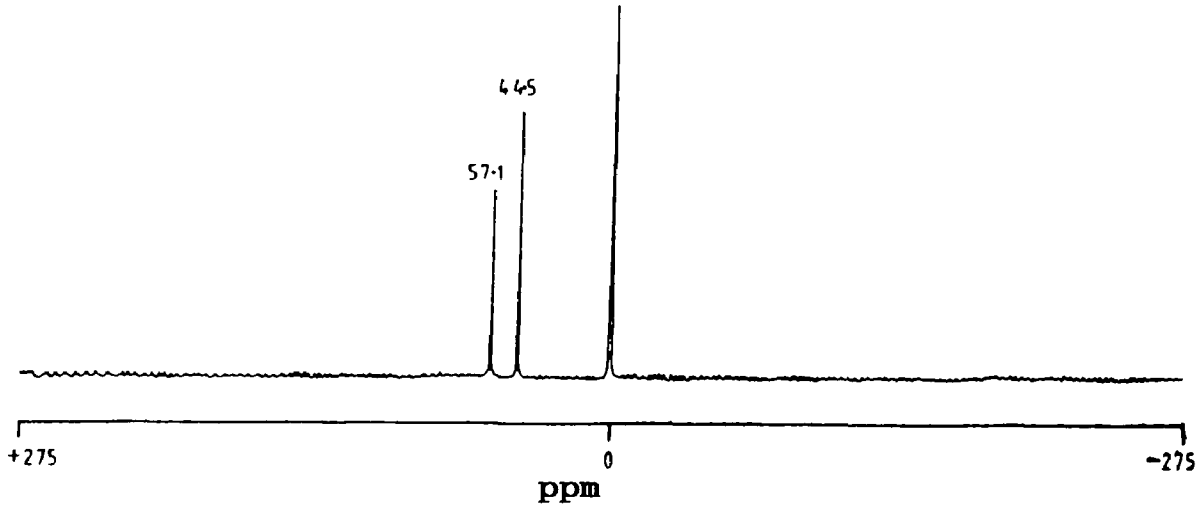


Figure 34 : ^{31}P-NMR spectrum of the protonated product of [Ni(CO)(dppe-PP')(dppe-P)] (in $CDCl_3$, 85% H_3PO_4)

M. J. Hudson et al.[98] have reported that the action of gaseous HCl on the substituted dicarbonyl [$Ni(CO)_2$(diarsine)] forms a complex [$NiCl_2$(diarsine)] (diarsine = 2-phenylenebisdimethylarsine). Therefore, [$NiCl_2$(dppe-PP')] may be produced as one component of the mixture in the present reaction. Alternatively, Schunn[76] reports that an HCl_2^- salt might be formed that decomposes to give H_2 and [$NiCl_2$(dppe-PP')]. Since the singlet δ 57.1 has been assigned for [$NiCl_2$(dppe-PP')], so the other singlet resonance observed at δ 44.5 (s) may be suggested for the phosphorus atoms of the nickel hydride complex. This singlet in the proton decoupled spectrum appearance indicates a single environment of phosphorus atoms in the complex. W. C. Drinkard et al.[75] have also synthesized a five coordinate stable nickel

hydride complex $[NiH\{P(OEt)_3\}_4]^+$ by the addition of strong acids to $[Ni\{P(OEt)_3\}_4]$ which shows a doublet at δ -135.0 in the ^{31}P-NMR spectrum. The authors have indicated that the ^1H-NMR and ^{31}P-NMR evidence could be interpreted that all four phosphorus atoms in the hydride molecules are equivalent, in which case a five coordinate square pyramidal geometry with the hydrogen at the apex would be indicated. However, they have not eliminated the possibility either that the chemical shifts and spin-spin coupling constants of a less symmetric structure (trigonal bipyramidal) are fortuitously very similar or that there is a very fast rate process of exchange between nonequivalent phosphorus atoms. They observed no broadening of the resonance on cooling to -60 ^0C.

The formation of the protonated product of this reaction may be analogous to product of the reaction of $[Ni\{P(OEt)_3\}_4]$ with strong acids[75] and have similar structure. This type of protonation may be regarded either as an oxidative addition of a proton to Ni(O) to give a formally nickel(II) hydride complex or as protonation of a Ni(O) complex[76].

Therefore, the reaction of [Ni(CO)(dppe-PP')(dppe-P)] with gaseous HCl is proposed to form two complexes; one is a stable nickel hydride complex the structure of which can not be definitely characterized and the other one is suggested as $[NiCl_2(dppe\text{-}PP')]$.

(h). Reaction of [Ni(CO)(dppe-PP')(dppe-P)] with Air : Formation of [Ni(dppe-PP')$_2$]

Reaction of [Ni(CO)(dppe-PP')(dppe-P)] with air apparently resulted in the formation of a mixture of products. A green component was not soluble in organic solvents. It is presumed to be a nickel decomposition product. A component soluble in organic solvents has been characterized as [Ni(dppe-PP')$_2$].

The infrared of the product soluble in organic solvents (KBr disc) (figure 35) shows no significant bands for ν(CO). The spectrum gives ν(C-H) (aromatic) and ν(C-H) (aliphatic) at 3055 (s) and 2943 (s) cm^{-1} respectively. ν(P-Ph)[86,87] is observed at 1439 (s) cm^{-1}. No bands are observed for ν(P=O)[88] between 1200-1300 cm^{-1}.

The ^{31}P-NMR spectrum (figure 36) of the soluble product shows one singlet resonance at δ 32.6 which has been identified for the four equivalent phosphorus atoms in [Ni(dppe-PP')$_2$] [section 4.4.(e).]. R. J. Puddephatt[35] has reported that dppe acts as an excellent chelate ligand because it forms a stable five membered ring to the metal in the complex. [Ni(dppe-PP')$_2$] would contain two such rings. This could account for the formation of [Ni(dppe-PP')$_2$] rather than the formation of any other oxidized products.

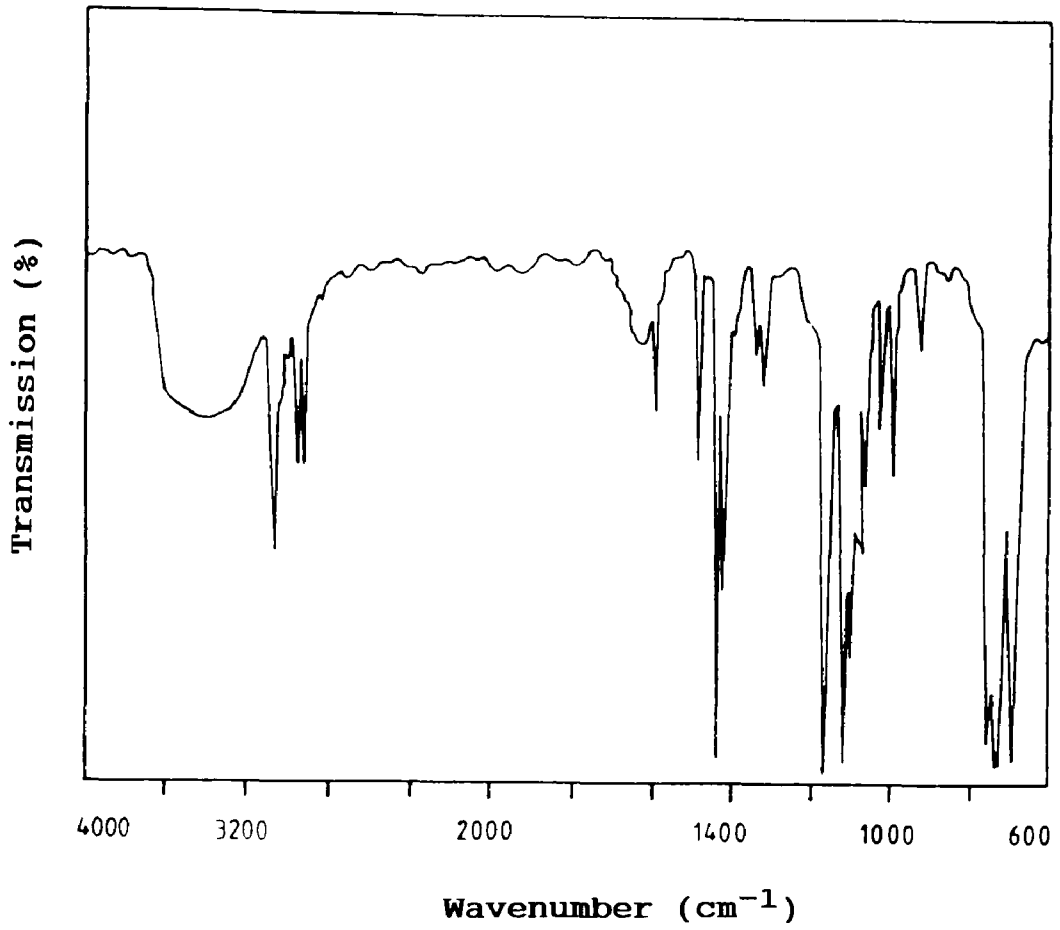


Figure 35 : IR spectrum of product of reaction 4.4.(h). (KBr disc)

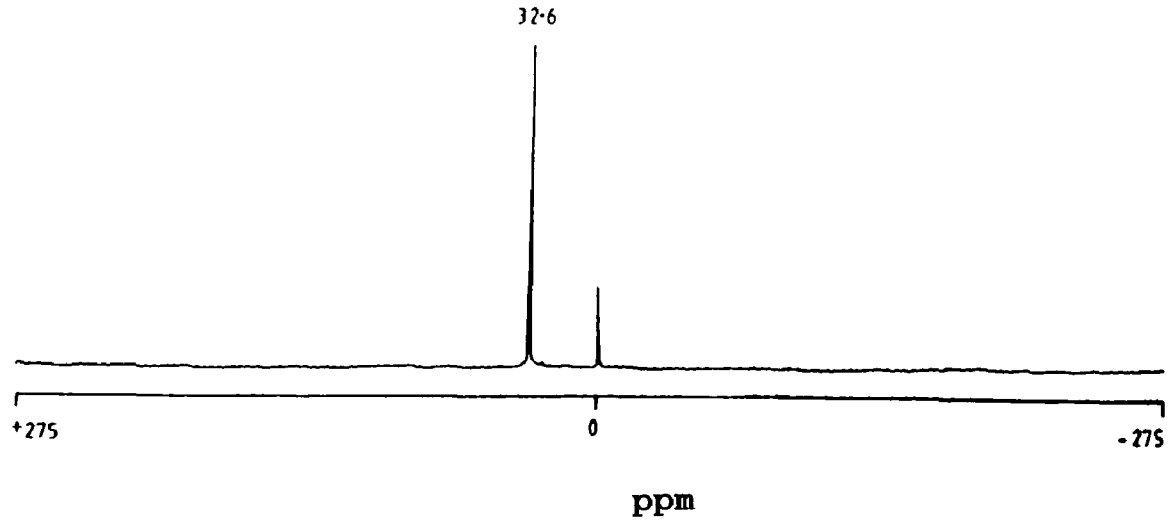


Figure 36 : ^{31}P-NMR spectrum of product of reaction 4.4.(h). (in $CDCl_3$, 85% H_3PO_4)

Therefore, it appears that Ni(CO)(dppe-PP')(dppe-P)], on exposure to air, loses CO and produces [Ni(dppe-PP')$_2$].

(i). Reaction of [Ni(CO)$_2$(dppm-P)$_2$] with Air : Formation of monoxide and dioxide of dppm, [Ph$_2$P(O)CH$_2$PPh$_2$] and [Ph$_2$P(O)CH$_2$P(O)Ph$_2$]

The reaction of [Ni(CO)$_2$(dppm-P)$_2$] with air leads to the formation of a mixture of products. A component of the mixture, soluble in organic solvents has been characterized as a mixture of the monoxide and dioxide of dppm, [Ph$_2$P(O)CH$_2$PPh$_2$] and [Ph$_2$P(O)CH$_2$P(O)Ph$_2$] respectively. A green component, insoluble in organic solvents, has been assumed to be a nickel decomposition product. G. Wilke et al.[70] have reported that [Ni(PPh$_3$)$_4$] reacts with oxygen at -78 ^{0}C to form [NiO$_2$(PPh$_3$)$_2$] containing a  ring which decomposes above -35 ^{0}C to nickel metal and triphenylphosphine oxide. The present reaction has been done at room temperature. Therefore, if an adduct of the type [NiO$_2$(dppm-P)$_2$] forms it could possibly decompose at room temperature to nickel metal and oxides of dppm. The infrared spectrum of the product did not show any band around 898 cm^{-1} for ν(O-O)[74].

The infrared spectrum of the soluble component of the product (KBr disc) (figure 37) shows no band for ν(CO). ν(C-H) (aromatic) and ν(C-H) (aliphatic) are observed at 3054 (s) and 2930 (s) cm^{-1} respectively. ν(P-Ph)[86,87]

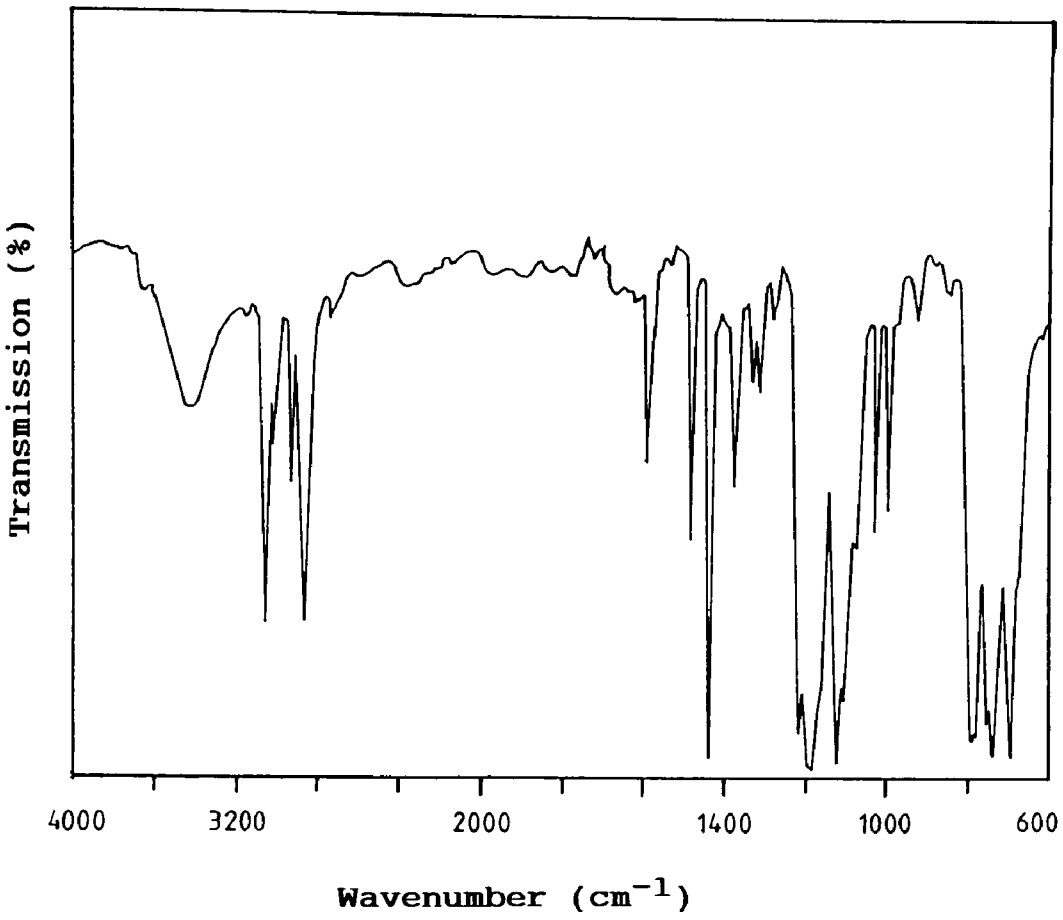


Figure 37 : IR spectrum of product of reaction 4.4.(i). (KBr disc)

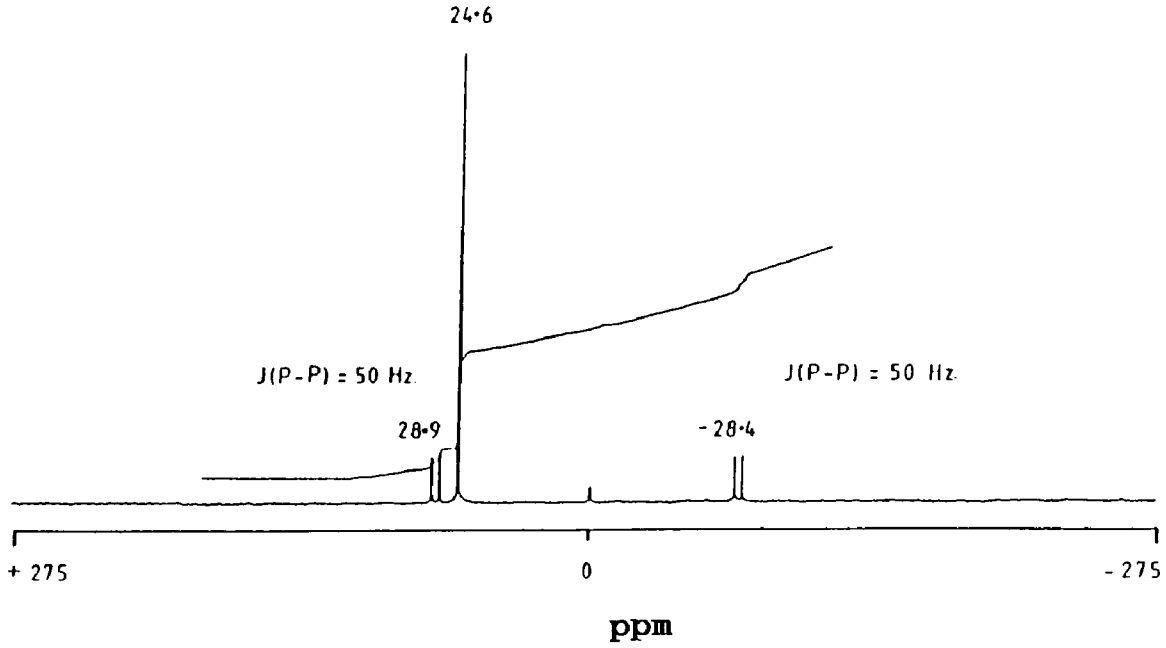


Figure 38 : ^{31}P-NMR spectrum of product of reaction 4.4.(i). (in $CDCl_3$, 85% H_3PO_4)

has been observed at 1437 (s) cm^{-1}. The IR spectrum also shows a sharp band at 1215 cm^{-1} which has been identified for $\nu(P=O)$[88]. This band is absent in the IR spectrum of free dppm and $[Ni(CO)_2(dppm\text{-}P)_2]$.

The ^{31}P-NMR spectrum of the product (figure 38) exhibits two doublet and one sharp singlet resonances. These indicate a different environment of phosphorus atoms present in the reaction product. The low field doublet resonance found at δ 28.9 ($^2J(P\text{-}P)$ 50 Hz)[89] has been assigned to the phosphorus atom bonded to the oxygen in the monoxide of dppm, $[Ph_2P(O)CH_2PPh_2]$. The high field doublet resonance observed at δ -28.4 ($^2J(P\text{-}P)$ 50 Hz)[89] is identified for the free phosphorus atom of $[Ph_2P(O)CH_2PPh_2]$. The integration ratio of these two doublets is found to be 1:1. The very sharp singlet resonance at δ 24.6 has been identified for two equivalent phosphorus atoms of the dioxide of dppm[89], $[Ph_2P(O)CH_2P(O)Ph_2]$. Recently, D. G. Holah et el.[9] reported the reactivity of a zerovalent nickel-carbonyl-phosphine complex towards O_2. He has found that $[Ni_2(CO)_3(dppm\text{-}P)_3]$ is very reactive towards trace amounts of O_2 to form the monoxide of dppm. P. Giannoccaro et al.[102] have also reported that the Ni(O)-carbonyl-phosphine complexes of formula $[Ni(CO)_{4-x}L_x]$ (x = 1, 2, L = PEt_3, PEt_2Ph) are oxidized by oxygen in acidic medium to Ni(II) phosphine complexes, CO_2 and phosphine oxide. It is also reported[70-74] that triphenylphosphine oxide can be

formed in the oxidation of $[M(PPh_3)_4]$ (M = Ni, Pd, Pt). So, previous reports agree with the suggestion that during the reaction of $[Ni(CO)_2(dppm\text{-}P)_2]$ with O_2, oxides of dppm can be formed. In the reaction of [Ni(CO)(dppe-PP')(dppe-P)] with air $[Ni(dppe\text{-}PP')_2]$ is the product. No equivalent dppm complex is formed in this instance. R. J. Puddephatt[35] has reported that in forming chelate complexes, the optimum ring size for a metal having natural bond angles at 90^0 to one another is five and dppe is an excellent chelate ligand in that sense because it forms a stable five membered ring to the metal in the complex. However, dppm can chelate but the four membered ring so formed is strained, leading to instability.

Therefore, $[Ni(CO)_2(dppm\text{-}P)_2]$ on reaction with air loses CO and gives a mixture of monoxide, $[Ph_2P(O)CH_2PPh_2]$ and dioxide, $[Ph_2P(O)CH_2P(O)Ph_2]$ of dppm and an insoluble species assumed to be a nickel decomposition product.

4.5. CONCLUSION

It has been mentioned in the introduction of the [section 4.1.] that [Ni(CO)(dppe-PP')(dppe-P)] and $[Ni(CO)_2(dppm\text{-}P)_2]$ would appear to be reasonable precursor compounds for the synthesis of Ni(II) organo derivatives via oxidative addition reactions with acyl halides, aroyl halides, alkyl and aryl halides. But it has been found experimentally that no Ni(II) organometallic derivatives could not be isolated from the said reactions, but these reactions produce only bis halo Ni(II) derivatives of the type[69] MX_2L_2 where M = Ni(II), L = chelate dppe or dppm, X = halogen.

Chatt and Shaw[84] have reported on the stability of the organometallic derivatives of the heavier transition metals, (Pd and Pt) and the lighter transition metal, (Ni). The heavier transition metal complexes (Pt and Pd) have greater double bonding and ligand field splitting than that of the corresponding Ni complexes and therefore Pt and Pd metals should form more stable organometallic compounds having occupied non-σ-bonding d orbitals (figure 12)[103-105]. For example, when stable complexes of the type $[MX_2(PR_3)_2]$ (M = Ni, Pd and Pt; X = halogen) of square planar configuration are treated with Grignard reagents, the stable organometallic derivatives of the three metals are isolated whose stabilities fall rapidly in the order Pt > Pd > Ni in accordance with the view discussed above[84].

Also, Malatesta et al.[69] have reported that oxidative addition reactions of alkyl, aryl or aroyl halides to the zerovalent metal phosphine compounds (ML_4) depend upon the reaction conditions and in some cases the organic part is not present in the reaction products, just simply bis halo derivatives. In the reaction of the zerovalent nickel complex $[Ni(PPh_3)_4]$ with benzoyl chloride[11], the aroyl derivative can not be isolated since the product spontaneously loses CO and $[NiClPh(PPh_3)_2]$ is isolated from the reaction. These experimental results suggest that nickel-aroyl derivatives are not stable as those of Pd(II) or Pt(II) derivatives. Oxidative addition[14] of R-X (R = Me, Et, CH_2Ph, X = Cl, Br, I) to $[Pt(CO)_2(phosphine)]$ (phosphine = PPh_3, dppe, dppb, dppm) produce both bis halo Pt(II) and organometallic products. A mechanism[14] for the formation of $[PtX_2(phosphine)]$ and [PtXR(phosphine)] from the reaction of $[Pt(CO)_2(phosphine)]$ and R-X has been reported. On the basis of this mechanism, the following pathway may be proposed for the reactions of Ni(O) complexes with alkyl and aryl halides.

$[Ni(CO)_2(phosphine)] \rightleftharpoons [Ni^{O}(phosphine)] + 2CO$

$[Ni^{O}(phosphine)] + R\text{-}X \rightleftharpoons [Ni^{I}X(phosphine)] + R\cdot$

$R\cdot + [Ni^{I}X(phosphine)] \longrightarrow [Ni^{II}XR(phosphine)]$

(would be a proposed route for the formation of the organometallic species)

$[Ni^{I}X(phosphine)] + R\text{-}X \longrightarrow [Ni^{II}X_2(phosphine)] + R\cdot$

(this reaction seems to be the most favoured for the Ni species)

Equation 39

Therefore, in the reactions of alkyl, acyl, aryl and aryl halides with the zerovalent nickel-carbonyl-diphosphine complexes stable organometallic derivatives are not formed.

SECTION 5

APPLICATION OF Ni(O)-CO-DIPHOSPHINE COMPLEXES TO THE SYNTHESIS OF HETEROBIMETALLIC SYSTEMS

5.1. INTRODUCTION

There is potential for the use of the Ni(O) complexes[10] $[Ni(CO)_2(dppm\text{-}P)_2]$ and [Ni(CO)(dppe-PP')(dppe-P)] in the synthesis of bimetallic systems[35,106-111]. Dppm can chelate but the four membered ring so formed is strained and the ligand has a greater tendency to act either as monodentate or as a bridging bidentate ligand[35]. The chelating tendency decreases as the chain length increases, so that for the ligands $Ph_2P(CH_2)_nPPh_2$ chelation is greatest for n = 2. A particularly good example is seen in the complex $[RhCl(CO)\{Ph_2P(CH_2)_nPPh_2\}]$ which exhibits dimeric behaviour when n = 1, 3 or 4 but is a monomer[112] when n = 2. Therefore, dppm has the ability to form bridged heterobimetallic as well as homobinuclear complexes. Complexes containing two *trans* bridging dppm are most common in rhodium(I) complexes[15,113-119], e. g., $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$. Heterobimetallic complexes include[10,111-112,120-121] $[NiPtCl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$, $[HgNiX_2(RC{\equiv}C)_2(\mu\text{-}dppm)_2]$, and $[MoNi(CO)_4(\eta^5\text{-}C_5H_5)(\mu\text{-}SPh)(\mu\text{-}dppm)]$. Dppe can also act as a bridging ligand[122], e.g., $[MoWCl_4(\mu\text{-}dppe)_2]$ but has a greater tendency to chelate. Because metal-phosphorus bonds are often very strong, the bridging diphosphine ligand can lock together two metal atoms in close proximity and hence promote organometallic reactions involving two metal centres.

Heterobimetallic complexes, with diphosphine ligands that contain metals with very different redox potentials represent interesting systems to study. For this reason, attempts were made to synthesize complexes containing nickel(O) and one other transition metal. The study of heterobimetallic complexes can lead to greater understanding of the reactions in both homogeneous and heterogeneous catalysis[1].

D. G. Holah et al.[10] have mentioned recently that $[Ni(CO)_2(dppm\text{-}P)_2]$ has potential in the synthesis of heterobimetallic complexes and indeed it appears to react very rapidly with, for example $[PtCl_2(COD)]$, $[NiCl_2.6H_2O]$, $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ and $[Mo((CO)_5THF]$. They reported isolation of a Ni-Pt heterobimetallic complex[10] $[NiPtCl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ formed by the reaction of $[Ni(CO)_2(dppm\text{-}P)_2]$ with $[PtCl_2(COD)]$. Also, L. Manojlovic-Muir et al.[123] reported the reaction of $[Ni(CO)_2(dppm\text{-}P)_2]$ with $NiCl_2.6H_2O$ to give a dppm-bridged dinuclear nickel complex, $[Ni_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$.

Therefore, the reactions of $[Ni(CO)_2(dppm\text{-}P)_2]$ and $[Ni(CO)(dppe\text{-}PP')(dppe\text{-}P)]$ with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$, $[Mo(CO)_3(C_7H_8)]$, $[Mo(CO)_3(MeCN)_3]$, $[PdCl_2(COD)]$ and $[W(CO)_4(MeCN)_2]$ were studied to investigate whether they could produce heterobimetallic complexes. Acetonitrile is a labile ligand, weakly coordinated to the metal and may be substituted by the free phosphorus atoms of the

monodentate dppm ligands of $[Ni(CO)_2(dppm\text{-}P)_2]$. Similarly, the olefinic ligands 1,7-cycloheptatriene and 1,5-cyclooctadiene are also weakly coordinated to the metal and thereby might be easily substituted by the free phosphorus atoms of the diphosphine ligands of the Ni(O) complexes.

5.2. HETEROBIMETALLIC SYNTHESIS USING DPPM

Some examples of the synthesis of heterobimetallic complexes using dppm are given below :

(a). Synthesis of a Ni-Mo Heterobimetallic Complex

When $[Ni(\eta^5\text{-}C_5H_5)(SPh)(dppm\text{-}P)]$ reacts with $[Mo(CO)_4(C_7H_8)]$, the free phosphorus atom in dppm of the complex coordinates with Molybdenum[120-121] (figure 39).

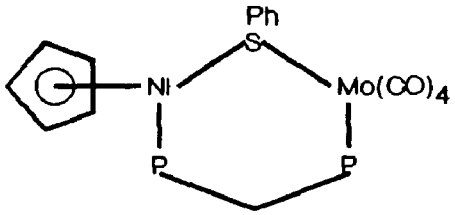


Figure 39 : Structure of $[MoNi(CO)_4(\eta^5\text{-}C_5H_5)(\mu\text{-}SPh)(\mu\text{-}dppm)]$

(b). Reaction of $[Ni(CO)_2(dppm\text{-}P)_2]$ with $[PtCl_2(COD)]$

$[Ni(CO)_2(dppm\text{-}P)_2]$ reacts very rapidly with $[PtCl_2(COD)]$ in CH_2Cl_2 at room temperature giving purple crystals[10] of $[NiPtCl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ (figure 40).

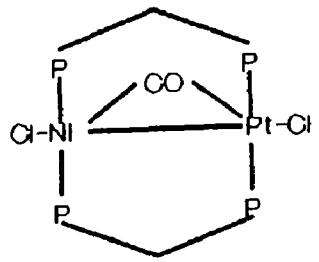


Figure 40 : Structure of $[NiPtCl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$

(c). Synthesis of $[PtW(CO)_3(RC{\equiv}C)_2(\mu\text{-dppm})_2]$ (R = Me, Ph or 4-tolyl)

These heterobimetallic complexes are prepared by the action[124] of *trans*-$[Pt(RC{\equiv}C)_2(dppm\text{-}P)_2]$ on fac-$[W(CO)_3(MeCN)_3]$ (figure 41)(R = Me, Ph or 4-tolyl).

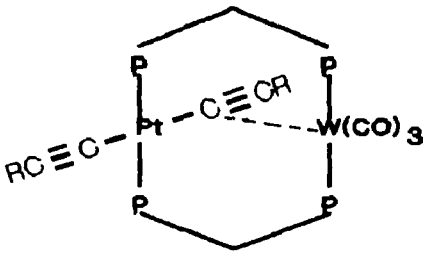
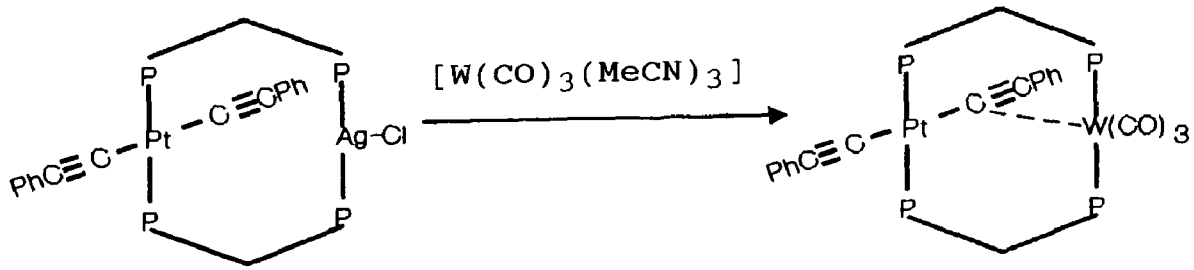


Figure 41 : Structure of $[PtW(CO)_3(RC{\equiv}C)_2(\mu\text{-dppm})_2]$

(d). Preparation[125] of μ-dppm Platinum(II)-Tungsten(0), -Molybdenum(0) or -Chromium(0) Complexes

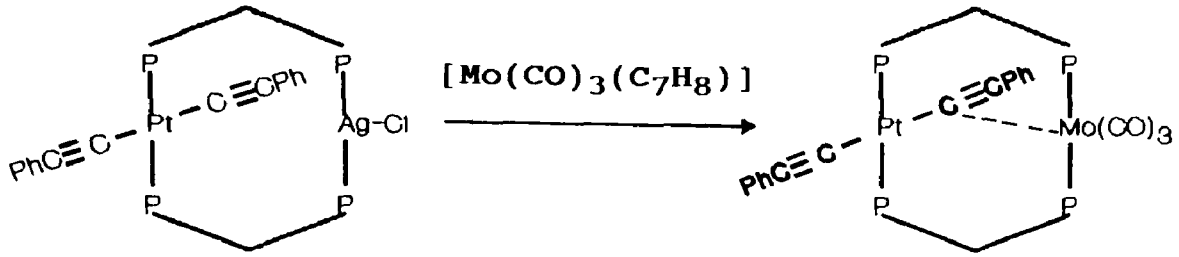
$[PtW(CO)_3(PhC{\equiv}C)_2(\mu\text{-dppm})_2]$ is obtained by the reaction of $[AgPtCl(PhC{\equiv}C)_2(\mu\text{-dppm})_2]$ with fac-$[W(CO)_3(MeCN)_3]$ in boiling benzene (equation 40).



Equation 40

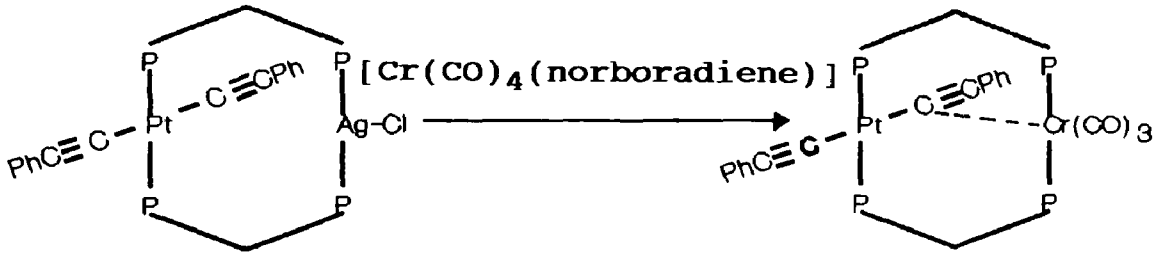
Treatment of $[Mo(CO)_3(C_7H_8)]$ with an equivalent amount of $[AgPtCl(PhC{\equiv}C)_2(\mu\text{-dppm})_2]$ in boiling benzene gives

$[MoPt(CO)_3(PhC{\equiv}C)_2(\mu\text{-dppm})_2]$ as orange red crystals (equation 41).



Equation 41

Treatment of $[Cr(CO)_4(norboradiene)]$ with $[AgPtCl(PhC{\equiv}C)_2(\mu\text{-dppm})_2]$ in refluxing benzene gives $[CrPt(CO)_3(PhC{\equiv}C)_2(\mu\text{-dppm})_2]$ (equation 42).



Equation 42

(e). Heterobimetallic Complexes of Palladium with Mercury, Silver, Rhodium, Iridium or Molybdenum Containing dppm[126]

Treatment of $[Pd(dppm\text{-}PP')_2]_2Cl_2$ with $Hg(C{\equiv}CPh)_2$ in CD_2Cl_2 at -40 ^0C gives the heterobimetallic complex $[HgPdCl_2(PhC{\equiv}C)_2(\mu\text{-dppm})_2]$ (figure 42).

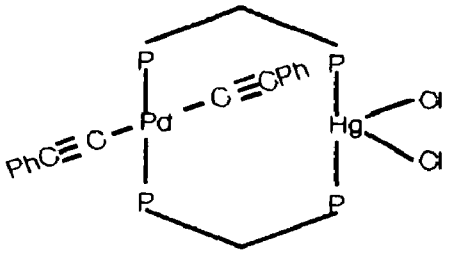


Figure 42 : Structure of $[HgPdCl_2(PhC{\equiv}C)_2(\mu\text{-dppm})_2]$

This complex decomposes at ca. +20 ^{0}C but when prepared in acetone-ethanol (1:1) at ca. -20 ^{0}C and then treated in situ with an equivalent amount of sodium sulfide in ethanol at or below 0 ^{0}C it gives mercuric sulfide and trans-$[Pd(C{\equiv}CPh)_2(dppm\text{-}P)_2]$ (figure 43).

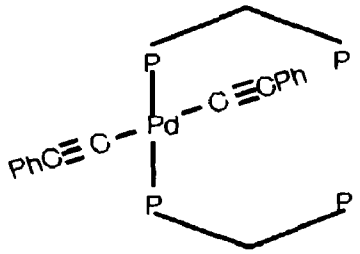
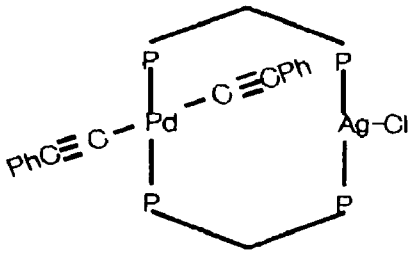
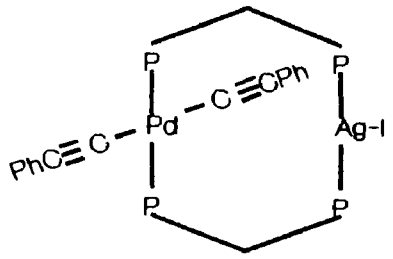


Figure 43 : Structure of *trans*-$[Pd(C{\equiv}CPh)_2(dppm\text{-}P)_2]$

When treated with $[AgCl(PPh_3)]_4$ in CH_2Cl_2 the dppm-P complex (figure 43) gives the palladium-silver complex $[AgPdCl(PhC{\equiv}C)_2(\mu\text{-dppm})_2]$ (figure 44). The corresponding silver iodide complex $[AgPdI(PhC{\equiv}C)_2(\mu\text{-dppm})_2]$ (figure 45) is similarly made using $[AgI(PPh_3)]_4$.



44

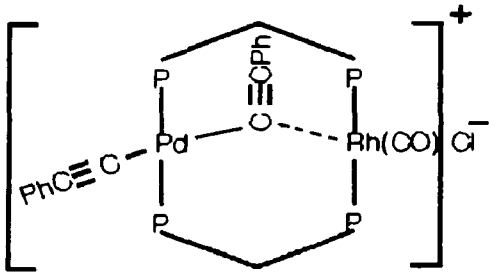


45

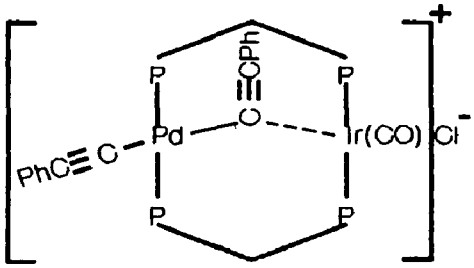
Figure 44 : Structure of $[AgPdCl(PhC{\equiv}C)_2(\mu\text{-dppm})_2]$

45 : Structure of $[AgPdI(PhC{\equiv}C)_2(\mu\text{-dppm})_2]$

Treatment of $[Pd(C{\equiv}CPh)_2(dppm\text{-}P)_2]$ (figure 6) with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ in CH_2Cl_2 gives the orange salt $[PdRh(CO)(PhC{\equiv}C)_2(\mu\text{-dppm})_2]Cl$ (figure 46) and with $[Ir_2Cl_2(cyclooctene)_4]$ followed by CO gives the corresponding iridium salt (figure 47).



46



47

Figure 46 : Structure of $[PdRh(CO)(PhC{\equiv}C)_2(\mu\text{-dppm})_2]Cl$

47 : Structure of $[IrPd(CO)(PhC{\equiv}C)_2(\mu\text{-dppm})_2]Cl$

A mixed Pd-Ag complex $[AgPdCl(PhC{\equiv}C)_2(\mu\text{-dppm})_2)]$ (figure 44) reacts with $[Mo(CO)_3(C_7H_8)]$ to give the deep red Pd-Mo complex $[MoPd(CO)_3(PhC{\equiv}C)_2(\mu\text{-dppm})_2]$ (figure 48).

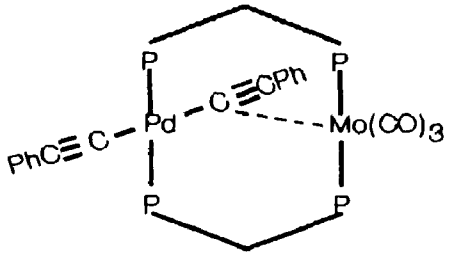


Figure 48 : Structure of $[MoPd(CO)_3(PhC{\equiv}C)_2(\mu\text{-dppm})_2]$

Treatment of $[AgPdCl(PhC{\equiv}C)_2(\mu\text{-dppm})_2]$ with fac-$[W(CO)_3(MeCN)_3]$ in CH_2Cl_2/CD_2Cl_2 gives the Pd-W analogue $[PdW(CO)_3(PhC{\equiv}C)_2(\mu\text{-dppm})_2]$ (figure 49).

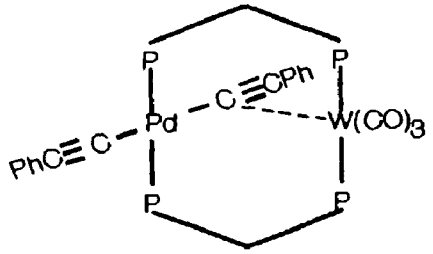
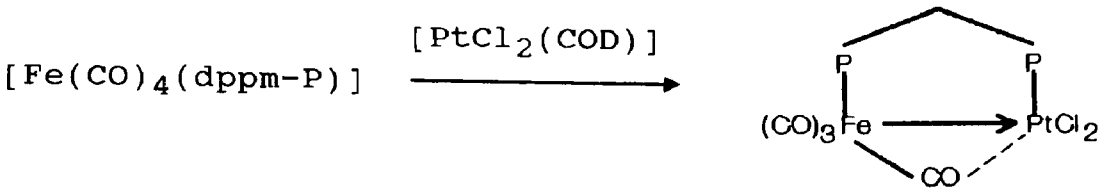


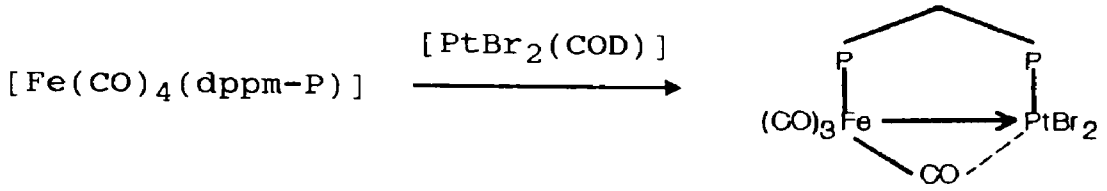
Figure 49 : Structure of $[PdW(CO)_3(PhC{\equiv}C)_2(\mu\text{-dppm})_2]$

(f). Synthesis of a Fe-Pt Heterobimetallic Complex

Treatment[127-128] of $[Fe(CO)_4(dppm\text{-}P)]$ with one mole equivalent of $[PtCl_2(COD)]$ in benzene-dichloromethane gives the iron-platinum heterobimetallic complex[129] $[FePtCl_2(CO)_3(\mu\text{-}CO)(\mu\text{-dppm})]$ (equation 43). The corresponding dibromide[129] $[FePtBr_2(CO)_3(\mu\text{-}CO)(\mu\text{-dppm})]$ (equation 44) is similarly prepared using $[PtBr_2(COD)]$.



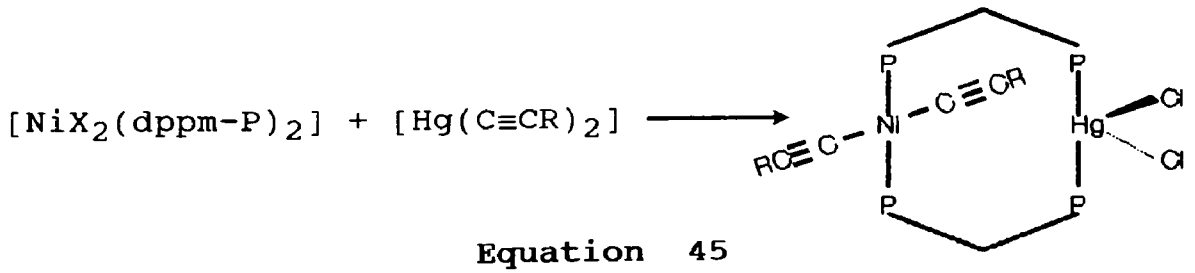
Equation 43



Equation 44

(g). Synthesis of Ni-Hg Heterobimetallic Systems

Treatment of red purple $[NiX_2(dppm\text{-}P)_2]$ (X = Cl, Br or I) in benzene or dichloromethane, with $Hg(C{\equiv}CR)_2$ (R = Ph or 4-tolyl) gives the yellow complex[111] $[HgNiX_2(RC{\equiv}C)_2(\mu\text{-}dppm)_2]$ (equation 45). With two equivalents of $[Au(PPh_3)(C{\equiv}CR)]$, the complex $[NiCl_2(dppm\text{-}P)_2]$ gives[111] $[AuNi(RC{\equiv}C)_2(\mu\text{-}dppm)_2]Cl$ (figure 50).



Equation 45

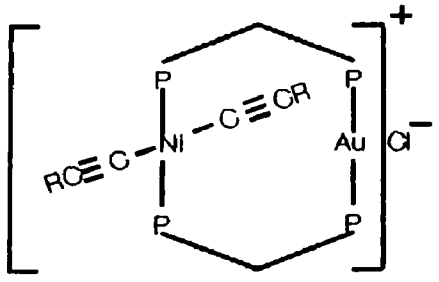
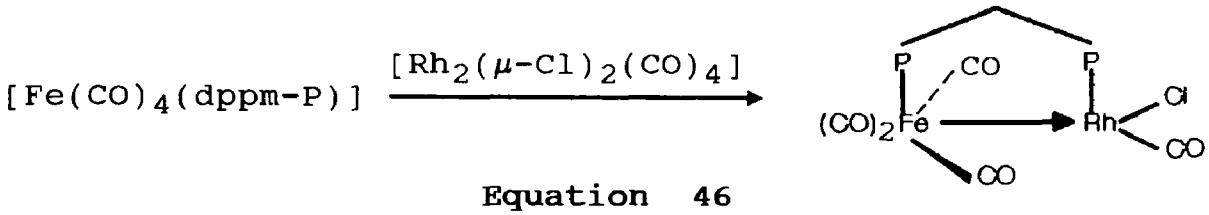


Figure 50 : Structure of $[AuNi(RC{\equiv}C)_2(\mu\text{-}dppm)_2]Cl$

(h). Synthesis of a Fe-Rh Heterobimetallic Complex containing bridging dppm

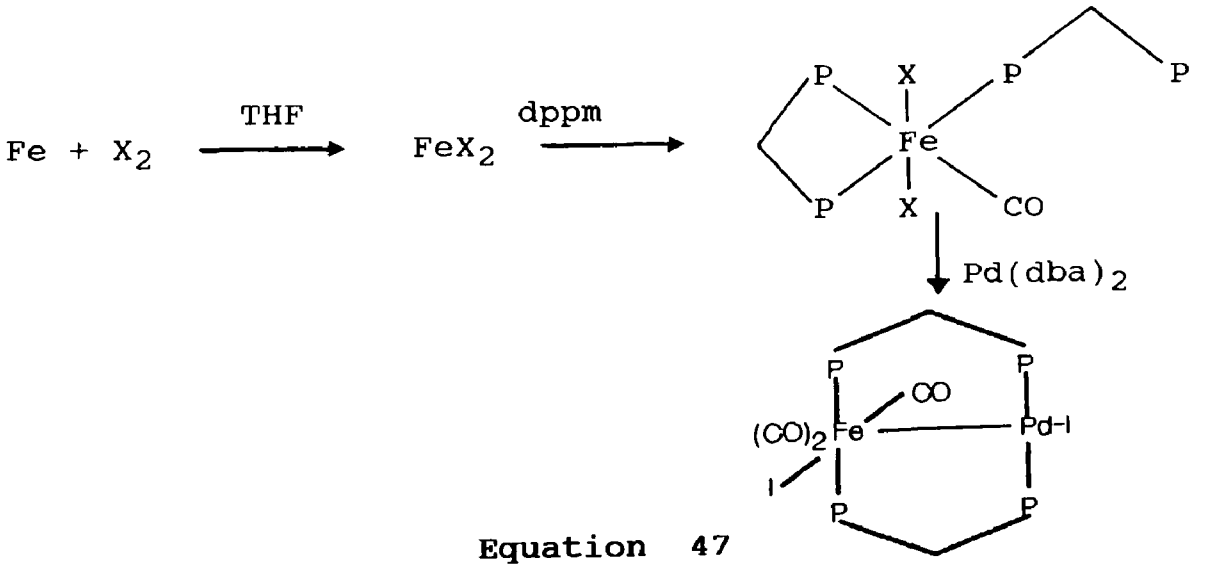
Treatment of $[Fe(CO)_4(dppm\text{-}P)]$ with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ in benzene gives the iron-rhodium heterobimetallic complex[107] $[FeRhCl(CO)_5(\mu\text{-}dppm)]$ (equation 46).



Equation 46

(i). Preparation of an Fe-Pd Heterobimetallic Complex

Treatment of THF solution of iron(II) iodide with two equivalents of dppm, under a CO atmosphere gives the iron(II) complex *trans*, mer-$[FeI_2(CO)(dppm\text{-}PP')(dppm\text{-}P)]$ which on treatment with $[Pd(dba)_2]$ in benzene under a CO atmosphere gives the bimetallic iron(I)-Palladium(I) complex[109] $[FePdI_2(CO)_3(\mu\text{-}dppm)_2]$ (equation 47).



Equation 47

(j). Synthesis of vinylidene- and phenylene- bridged Complexes of diNickel(II), Ni-Pd(II) and Ni-Pt(II) containing dppm[130]

Treatment of $[Ni(COD)_2]$, dppm (1:1.5) with $Cl_2C{=}CH_2$ gives the vinylidene-bridged "A" frame complex (figure 51). A better route to the synthesis of this complex involves the combination of $[Ni(COD)_2]$, dppm and *trans*-$[NiCl(ClC{=}CH_2)(PPh_3)_2]$ (1:2:1) in C_6H_6. Corresponding dibromide, diiodide or diisocyanate complexes (figures 52a, 52b and 52c) are formed by the treatment of this dinuclear complex with LiBr, NaI and KCNS respectively.

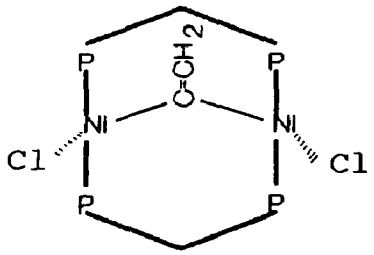
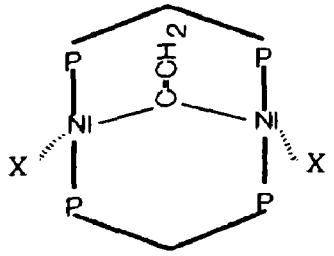


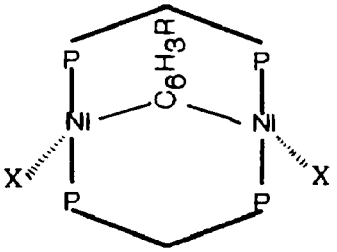
Figure 51 : Structure of $[Ni_2Cl_2(\mu\text{-}C{=}CH_2)(\mu\text{-dppm})_2]$



52a = Br
52b = I
52c = NCS

Figure 52 : Structure of $[Ni_2X_2(\mu\text{-}C{=}CH_2)(\mu\text{-dppm})_2]$

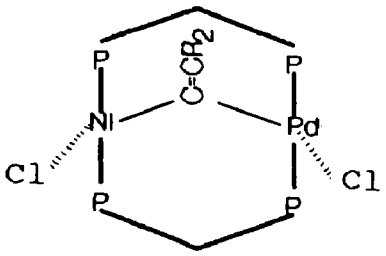
Phenylene or substituted phenylene-bridged A-frames of the type $[Ni_2X_2(\mu\text{-}C_6H_3R)(\mu\text{-dppm})_2]$ [X = Cl, R = H (figure 53a); X = Br, R = H (figure 53b); X = Cl, R = Me (figure 53c); X = Cl, R = OH (figure 53d)] have been synthesized using *trans*-$[NiX(C_6H_3RX)(PPh_3)_2]$.



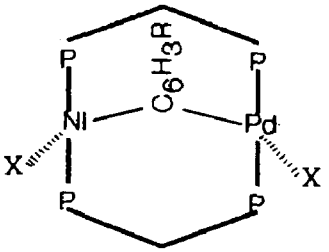
53a : X = Cl, R = H
53b : X = Br, R = H
53c : X = Cl, R = Me
53d : X = Cl, R = OH

Figure 53 : Structure of $[Ni_2X_2(\mu\text{-}C_6H_3R)(\mu\text{-dppm})_2]$

By treating these substituted vinyl or aryl nickel complexes, *trans*-$[NiX(ClC{=}CR_2)(PPh_3)_2]$ and *trans*-$[NiX(C_6H_3RX)(PPh_3)_2]$ with $[Pd(PPh_3)_4]$ and dppm, heterobimetallic A-frame complexes of the types $[NiPdCl_2(\mu\text{-}C{=}CR_2)(\mu\text{-dppm})_2]$ [R = H (figure 54a), R = Cl (figure 54b)] and $[NiPdX_2(\mu\text{-}C_6H_3R)(\mu\text{-dppm})_2]$ [X = Cl, R = H (figure 55a), X = Br, R = H (figure 55b)] have been obtained.



54a : R = H
54b : R = Cl



55a : X = Cl, R = H
55b : X = Br, R = H

Figure 54 : Structure of $[NiPdCl_2(\mu\text{-}C{=}CR_2)(\mu\text{-}dppm)_2]$

55 : Structure of $[NiPdX_2(\mu\text{-}C_6H_3R)(\mu\text{-}dppm)_2]$

By the reaction of $[Pt(PPh_3)_4]$ with dppm and $[NiCl(CCl{=}CCl_2)(PPh_3)_2]$ a Ni-Pt heterobimetallic complex $[NiPtCl_2(\mu\text{-}C{=}CCl_2)(\mu\text{-}dppm)_2]$ (figure 56) is formed.

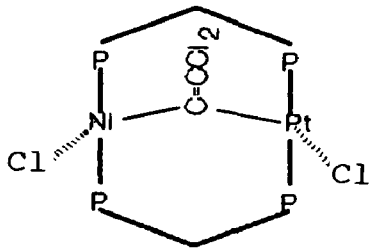
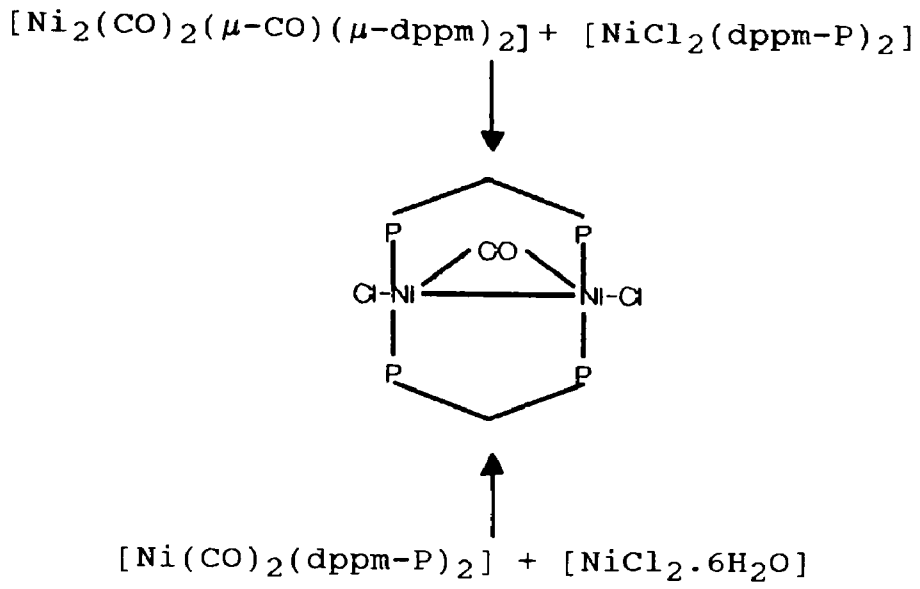


Figure 56 : Structure of $[NiPtCl_2(\mu\text{-}C{=}CCl_2)(\mu\text{-}dppm)_2]$

(k). Synthesis of a binuclear Nickel(I) Complex containing bridging dppm

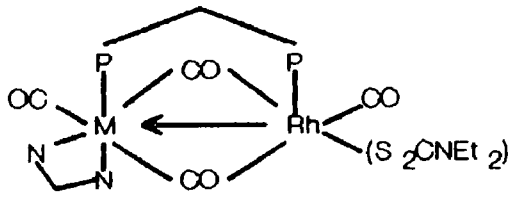
The reaction[123] of the zerovalent nickel complex $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ with $[NiCl_2(dppm\text{-}P)_2]$ or $[Ni(CO)_2(dppm\text{-}P)_2]$ with $NiCl_2.6H_2O$ produces $[Ni_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ (equation 48).



Equation 48

(1). Reactions[131] of $[Rh(CO)_2(S_2CNEt_2)]$ with the Complexes $[M(CO)_3(Phen\text{-}NN')(dppm\text{-}P)]$ (M = Mo or W) and $[Mo(CO)_4(dppm\text{-}PP')]$: Formation of Rh-Mo and Rh-W Heterobimetallic Complexes containing dppm ligands

Reactions of $[M(CO)_3(Phen\text{-}NN')(dppm\text{-}P)]$ (M = Mo and W) with $[Rh(CO)_2(S_2CNEt_2)]$ give heterobimetallic complexes $[MRh(CO)(Phen\text{-}NN')(S_2CNEt_2)(\mu\text{-}CO)_2(\mu\text{-}dppm)]$ (M = Mo and W) (figure 57).



(M = Mo or W)

Figure 57 : Structure of

$[MRh(CO)(Phen\text{-}NN')(S_2CNEt_2)(\mu\text{-}CO)_2(\mu\text{-}dppm)]$

$[Rh(CO)_2(S_2CNEt_2)]$ reacts with $[Mo(CO)_4(dppm\text{-}PP')]$ to give a Mo-Rh heterobimetallic complex $[MoRh(CO)_5(S_2CNEt_2)(\mu\text{-}dppm)]$ (figure 58).

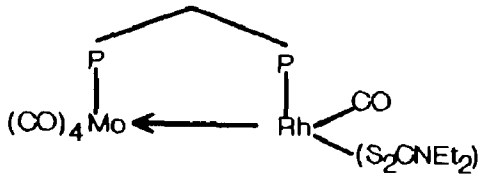
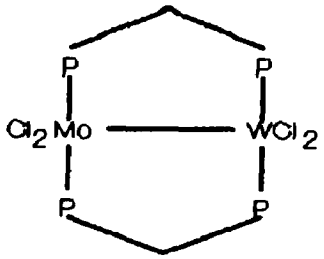


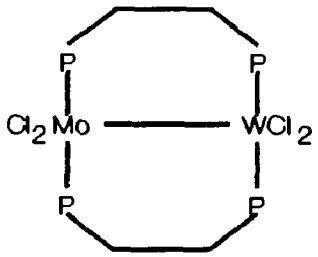
Figure 58 : Structure of $[MoRh(CO)_5(S_2CNEt_2)(\mu\text{-}dppm)]$

(m). Preparation and characterization of $[MoWCl_4(L\text{-}L)_2]$ (L-L = chelating dppe, dmpe) and $[MoWCl_4(L\text{-}L)_2]$ (L-L = bridging dppm, dmpm, dppe)[122]

When $[MoWCl_4(PMePh_2)_4]$ reacts with dppm, a Mo-W heterobimetallic complex containing bridging dppm $[MoWCl_4(\mu\text{-}dppm)_2.2THF.C_6H_6]$ (figure 59a) is formed. $[MoWCl_4(\mu\text{-}dppe)_2]$ (figure 59b) is formed by the reflux reaction of $[MoWCl_4(PMePh_2)_4]$ with dppe in 1-propanol. A Mo-W heterobimetallic complex containing the chelating dppe ligand, $[MoWCl_4(dppe\text{-}PP')_2]$ (figure 60) is formed from the reaction of $[MoWCl_4(PMePh_2)_4]$ and dppe in methanol at room temperature.



(a)



(b)

Figure 59 : Structures of (a). $[MoWCl_4(\mu\text{-}dppm)_2]$ (b). $[MoWCl_4(\mu\text{-}dppe)_2]$

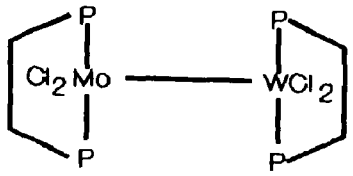


Figure 60 : Structure of $[MoWCl_4(dppe\text{-}PP')_2]$

With dmpm and dmpe $[MoWCl_4(PMePh_2)_4]$ give Mo-W complexes $[MoWCl_4(\mu\text{-}dmpm)_2]$ and $[MoWCl_4(dmpe\text{-}PP')_2]$ respectively.

5.3. EXPERIMENTAL PROCEDURES

(a). Preparation[132] of [$PdCl_2$(COD)]

The starting material [$PdCl_2$(COD)] was prepared following a known procedure[132]. A mixture of potassium tetrachloropalladate(II) (2.0 g, 6.16 mmol), water (80 cm^3), and 1,5-cyclooctadiene (2 cm^3) was shaken vigorously for 15 minutes, during which time a yellow solid was formed. This was then filtered, washed with water (10 cm^3 x 3) and dried in vacuo overnight at 40 ^0C to give [$PdCl_2$(COD)]. Yield, 1.06 g (60%).

IR (nujol) : 1454, 1417, 1347, 1080, 1001, 867, 822 cm^{-1}.

^{1}H-NMR ($CDCl_3$) : δ 6.32 (b, 4H olefinic protons), δ 2.65 (q, 8H CH_2 protons). These IR and ^{1}H-NMR values are in agreement with literature values[133] for [$PdCl_2$(COD)].

(b). Preparation of [$PtCl_2$(COD)]

Potassium tetrachloroplatinate(IV) (2.0 g, 4.8 mmol) was dissolved in water (50 cm^3) and then 1,5-cyclooctadiene (2 cm^3) was added to the solution. The reaction mixture was then stirred for 8 h at room temperature. A white solid was separated by filtration and washed with water (10 cm^3 x 3), then dried in vacuo overnight at 40 ^0C to give [$PtCl_2$(COD)]. Yield, 1.09 g (60 %).

IR (nujol) : 1338, 1179, 1009, 872, 832, 780 cm^{-1}.

^{1}H-NMR $CDCl_3$) : δ 5.61 (b, 4H olefinic protons), δ 2.65 (q, 8H CH_2 protons). IR and ^{1}H-NMR values reported here are in accordance with literature values[133] for $[PtCl_2(COD)]$.

(c). Preparation[134] of $[W(CO)_4(MeCN)_2]$

The complex $[W(CO)_6]$ (0.30 g, 0.85 mmol) was dissolved in acetonitrile (35 cm^3). The reaction mixture was then refluxed for 40 h under nitrogen. The solvent was removed under vacuo to give a greenish-yellow crude product. Dichloromethane (20 cm^3) was added to the crude product to produce a yellow solution. The solution was filtered and addition of diethyl ether (35 cm^3) to the concentrated filtrate (5 cm^3) resulted in the formation of a yellow precipitate. The product was separated by filtration and washed with diethyl ether (10 cm^3). The product was dried in vacuo and collected as yellow coloured crystals of $[W(CO)_4(MeCN)_2]$. Yield, 0.15 g (46 %).

IR (acetonitrile) : $\tilde{\nu}$(CO) at 2019 (m), 1893 (s) and 1835 (s) cm^{-1}. The colour and IR values of the product reported here are in agreement with the literature[135-136] for $[W(CO)_4(MeCN)_2]$.

(d). Reaction of $[Ni(CO)_2(dppm\text{-}P)_2]$ with $[PdCl_2(COD)]$: Synthesis of a Ni-Pd Heterobimetallic Complex, $[NiPdCl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ and a monomer Complex, $[PdCl_2(dppm\text{-}PP')]$

To a degassed solution of $[Ni(CO)_2(dppm\text{-}P)_2]$ (0.35 g, 0.40 mmol) in dry dichloromethane (15 cm^3), a degassed solution of $[PdCl_2(COD)]$ (0.12 g, 0.42 mmol) in the same solvent (10 cm^3) was added under nitrogen. The colour of the mixture immediately changed to dark blue. After 35-45 minutes the colour of the reaction mixture changed to green and a blue precipitate appeared. The product was collected by filtration and washed with diethyl ether (10 cm^3). Finally, it was dried for 30 minutes in vacuo. The product was found to be a mixture of a Ni-Pd heterobimetallic complex $[NiPdCl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$, $[PdCl_2(dppm\text{-}PP')]$ and $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$. The reaction was repeated at -18 ^0C and -50 ^0C. For -18 ^0C a mixture of ice, acetone and salt was used as coolant and for -50 ^0C a mixture of liquid nitrogen and ethyl acetate was used as coolant. For these reactions a blue coloured product was also obtained.

IR (KBr): $\bar{\nu}$(CO) (bridging) at 1786 (s) cm^{-1}.

^{31}P-NMR ($CDCl_3/H_3PO_4$) (room temperature) : δ 26.0 (d, ^2J(P-P) 34 Hz), δ 18.1 (d, ^2J(P-P) 34 Hz), δ -54.3 (s) $[PdCl_2(dppm\text{-}PP')]$, δ 23.9 (s) $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$.

(e). Reaction of [Ni(CO)(dppe-PP')(dppe-P)] with [$PdCl_2$(COD)] : Formation of [$NiCl_2$(dppe-PP')]

To a solution of [Ni(CO)(dppe-PP')(dppe-P)] (0.25 g, 0.28 mmol) in dichloromethane (10 cm^3) a solution of [$PdCl_2$(COD)] (0.08 g, 0.28 mmol) in the same solvent (18 cm^3) was added under nitrogen. The reaction mixture was then degassed and stirred under nitrogen at -18 ^0C (a mixture of ice, acetone and salt was used as coolant) for 45 minutes. A reddish black solution with a black precipitate was produced. The reaction mixture was then filtered and addition of dry diethyl ether to the concentrated filtrate (5 cm^3) gave an orange precipitate which was separated by filtration and washing with diethyl ether (10 cm^3). This product was dried in vacuo for 1 h. The black precipitate was not soluble in any organic solvent and IR (KBr disc) did not give any stretching band. The orange product was identified as [$NiCl_2$(dppe-PP')].

IR (KBr disc) : $\bar{\nu}$(CO) absent, $\bar{\nu}$(C-H) (aromatic) at 3050 (w) cm^{-1}, $\bar{\nu}$(C-H) (aliphatic) at 2910 (w) cm^{-1}, $\bar{\nu}$(P-Ph) at 1434 (s) cm^{-1}.

^{31}P-NMR ($CDCl_3$)/H_3PO_4 : δ 57.2 (s) for [$NiCl_2$(dppe-PP')].

(f). Reaction of $[Ni(CO)_2(dppm\text{-}P)_2]$ with $[PtCl_2(COD)]$: Preparation[10] of $[NiPtCl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$

To a degassed solution of $[Ni(CO)_2(dppm\text{-}P)_2]$ (0.30 g, 0.34 mmol) in dichloromethane (10 cm^3) was added a solution of $[PtCl_2(COD)]$ (0.12 g, 0.35 mmol) in the same solvent (10 cm^3). The reaction mixture was stirred for 4 h under nitrogen, during which a purple coloured precipitate was formed. The product was separated by filtration and washed with diethyl ether (10 cm^3) and finally dried in vacuo.

IR (KBr disc) : ν(CO) (bridging) at 1754 (s), ν(C-H) (aromatic) at 3051 (w), ν(C-H) (aliphatic) at 2922 (w) cm^{-1}, ν(P-Ph) at 1434 (s) cm^{-1}. ν(CO) is in agreement with the literature value[10].

^{31}P-NMR ($CDCl_3/H_3PO_4$) : δ 24.7 (s), δ -22.0 (b), δ -37.0 (s), δ -37.0 (d, J(Pt-P) 2030 Hz).

(g). Reaction of $[Ni(CO)(dppe\text{-}PP')(dppe\text{-}P)]$ with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$: Formation of a mixture of $[RhCl(CO)(dppe\text{-}PP')]$, $[RhCl(dppe\text{-}PP')_2]$ and $[Ni(dppe\text{-}PP')_2]$

$[Ni(CO)(dppe\text{-}PP')(dppe\text{-}P)]$ (0.50 g, 0.56 mmol) was dissolved in 15 cm^3 of degassed dichloromethane and a solution of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ (0.10 g, 0.25 mmol) in the same solvent (10 cm^3) was added. The reaction mixture was stirred for 3 h under nitrogen and filtered. Addition of diethyl ether to the concentrated filtrate

resulted in the formation of a bright yellow precipitate (5 cm^3) which was collected by filtration and washing with diethyl ether (5 cm^3 x 3). Finally the product was dried in a vacuo which was found to be a mixture of [RhCl(CO)(dppe-PP')], [RhCl(dppe-PP')$_2$] and [Ni(dppe-PP')$_2$].

IR (KBr disc) : $\tilde{\nu}$(CO) (terminal) at 2010 (s) cm^{-1}. Far IR (CsI disc) : $\tilde{\nu}$(Rh-Cl) (terminal) at 300 (b) cm^{-1}. The $\tilde{\nu}$(CO) (KBr) value at 2010 cm^{-1} and Far IR value of $\tilde{\nu}$(Rh-Cl) at 300 cm^{-1} are in agreement with the literature value of $\tilde{\nu}$(CO)[112] and $\tilde{\nu}$(Rh-Cl)[15] for [RhCl(CO)(dppe-PP')].

^{31}P-NMR ($CDCl_3/H_3PO_4$): δ 69.2 (dd) (^{3}J(P-P) 34 Hz), δ 47.5 (dd) (^{3}J(P-P) 34 Hz) (J(Rh-P), 127 and 160 Hz), in agreement with the literature[16,112] for [RhCl(CO)(dppe-PP')], δ 56.2 (d) (J(Rh-P) 132 Hz), agrees with the reported[16] value of [RhCl$_2$(dppe-PP')], δ 31.9 (s) [Ni(dppe-PP')$_2$].

(h). Reaction of [Ni(CO)$_2$(dppm-P)$_2$] with [Mo(CO)$_3$(C$_7$H$_8$] : Formation of [Ni$_2$(CO)$_2$(μ-CO)(μ-dppm)$_2$]

To [Ni(CO)$_2$(dppm-P)$_2$] (0.32 g, 0.36 mmol) in degassed dichloromethane (15 cm^3), under nitrogen was added [Mo(CO)$_3$(C_7H_8)] (0.10 g, 0.37 mmol) in dichloromethane (15 cm^3) via a transfer tube. The reaction mixture was stirred for 3-4 h under nitrogen. The reaction mixture was filtered under nitrogen, then concentrated to 5 cm^3 in vacuo. Addition of degassed diethyl ether (30 cm^3) by

a syringe gave a yellow precipitate which was separated by filtration, washed with diethyl ether (5 cm^3 x 3) and then dried in vacuo for 30 minutes.

IR (KBr disc) : broad bands for $\bar{\nu}$(CO) (terminal) in the range 2000-1940 cm^{-1} and $\bar{\nu}$(CO) (bridging) at 1782 cm^{-1}, in agreement with the literature[9] values of $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$.

^{31}P-NMR ($CDCl_3$)/H_3PO_4 : at room temperature, δ 22.2 (s) $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$. This value was also in agreement with the literature[9] value of $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$.

Formation of Crystals of $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$

The reaction product (0.70 g) was dissolved in the minimum volume of a mixture of dichloromethane and ethanol (3:1) (18 cm^3). The solution was kept overnight under a very slow flow of nitrogen which allowed the evaporation of the solvent. Slow evaporation of the solvent gave yellow crystals. These crystals were subjected to X-ray crystallography (appendix figure 15). This crystal structure has been previously reported[137].

(i). Reaction of [Ni(CO)(dppe-PP')(dppe-P)] with $[Mo(CO)_3(C_7H_8)]$: Preparation of $[Ni(dppe\text{-}PP')_2]$

To a degassed solution of [Ni(CO)(dppe-PP')(dppe-P)] (0.30 g, 0.34 mmol) in dichloromethane (15 cm^3) a degassed solution of $[Mo(CO)_3(C_7H_8)]$ (0.09 g, 0.34 mmol)

in the same solvent (10 cm^3) was added under nitrogen. The reaction mixture was stirred for 3 h under nitrogen. The reaction mixture was filtered and addition of diethyl ether (25 cm^3) to the concentrated filtrate (5 cm^3) gave a brown precipitate. The product was washed with diethyl ether (5 cm^3 x 3) and then dried in vacuo.
IR (KBr disc) : $\tilde{\nu}$(CO) (w) at 1922 and 1972 (w) cm^{-1}.
^{31}P-NMR ($CDCl_3/H_3PO_4$) : δ 32.7 (s).

(j). Reaction of $[Ni(CO)_2(dppm\text{-}P)_2]$ with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$: Formation of a mixture of *trans*-$[RhCl(CO)(\mu\text{-}dppm)]_2$ and $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$

To a degassed solution of $[Ni(CO)_2(dppm\text{-}P)_2]$ (0.23 g, 0.26 mmol) in dichloromethane (10 cm^3) a solution of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ (0.10 g, 0.25 mmol) was added. The reaction mixture was then stirred under nitrogen for 3 h. Concentration of the solvent to 5 cm^3 gave an orange-yellow precipitate which was filtered and washed with diethyl ether (5 cm^3 x 2). The product was dried in vacuo for 30 minutes.
IR (KBr disc) : $\tilde{\nu}$(CO) (terminal) at 1968 (s), (bridging) at 1760 (w) cm^{-1}. The $\tilde{\nu}$(CO) at 1968 cm^{-1} is in agreement with the literature[15,16,112] $\tilde{\nu}$(CO) value for $[RhCl(CO)(\mu\text{-}dppm)]_2$. The $\tilde{\nu}$(CO) (bridging) at 1761 also agrees with the literature[114] value for $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$.
^{31}P-NMR ($CDCl_3/H_3PO_4$) : The product was partially soluble in $CDCl_3$ and a good spectrum was not obtained.

Only δ 19.7 (d, J(Rh-P) 116 Hz) was found which agrees with the reported[114] value of $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$.

5.3. RESULTS AND DISCUSSION

(a). Rearrangement of $[Ni(CO)_2(dppm\text{-}P)_2]$ in solution

D. G. Holah et al.[10] have reported that $[Ni(CO)_2(dppm\text{-}P)_2]$ rearranges very rapidly in solution (unless the solution is cooled or an excess of free dppm present) to give[9,46-47] $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ which contains two terminal CO, one bridging CO and two bridging dppm ligands. It has been observed that when $[Ni(CO)_2(dppm\text{-}P)_2]$ is dissolved in CH_2Cl_2 (or any organic solvent) and the solution is left at room temperature, then within a few minutes the colour of solution changes from colourless to the yellow of $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$, the IR of which shows the disappearance of ν(CO) for $[Ni(CO)_2(dppm\text{-}P)_2]$ but a bridging $\bar{\nu}$(CO) at 1781 cm^{-1} and a broad band for terminal $\bar{\nu}$(CO) between 2000-1940 cm^{-1}. These values are consistent with the literature values[9] for $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$.

(b). Reaction of $[Ni(CO)_2(dppm\text{-}P)_2]$ with $[Mo(CO)_3(C_7H_8)]$: Crystal Structure of $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$

Attempts to prepare a Ni-Mo heterobimetallic complex by reacting $[Ni(CO)_2(dppm\text{-}P)_2]$ with $[Mo(CO)_3(C_7H_8)]$ resulted in no reaction between the complexes. Instead $[Ni(CO)_2(dppm\text{-}P)_2]$ rearranged in solution giving a dimer

$[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$. The yellow solid produced was characterized as $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$.

The infrared spectrum of the product (KBr disc) (figure 61) contains broad bands for terminal $\bar{\nu}$(CO) between 2000-1940 cm^{-1} and a sharp bridging $\bar{\nu}$(CO) at 1782 cm^{-1}, characteristic of bridging carbonyl stretching frequency. Values for $\bar{\nu}$(C-H) (aromatic), $\bar{\nu}$(C-H) (aliphatic) and $\bar{\nu}$(P-Ph)[86-87] have been observed at 3053 (w), 2927 (w) and 1434 (s) cm^{-1} respectively.

The ^{31}P-NMR spectrum of the yellow solid (at room temperature) (figure 62) shows two sharp singlet resonances at δ 22.2 and δ 17.7 . D. G. Holah et al.[9] reported the ^{31}P-NMR of $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ found at δ 22.7 as a singlet. They have also reported in the same paper[9] that another dimer $[Ni_2(CO)_3(dppm\text{-}P)_3]$ formed from the reaction of dppm with $NiCl_2.6H_2O$ and $NaBH_3CN$ as side product (main product is $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$) rapidly decomposes in solution at room temperature giving $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$, free dppm and a symmetrically bridged dppm species with a sharp singlet at δ 17 in the ^{31}P-NMR spectrum. They do not suggest the structure of this species. Crystals were grown from the product formed as in [section 5.3.(h).]. X-ray crystallography shows that the structure of the product is $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ (appendix figure 15). D. G. Holah et al.[10] reported that

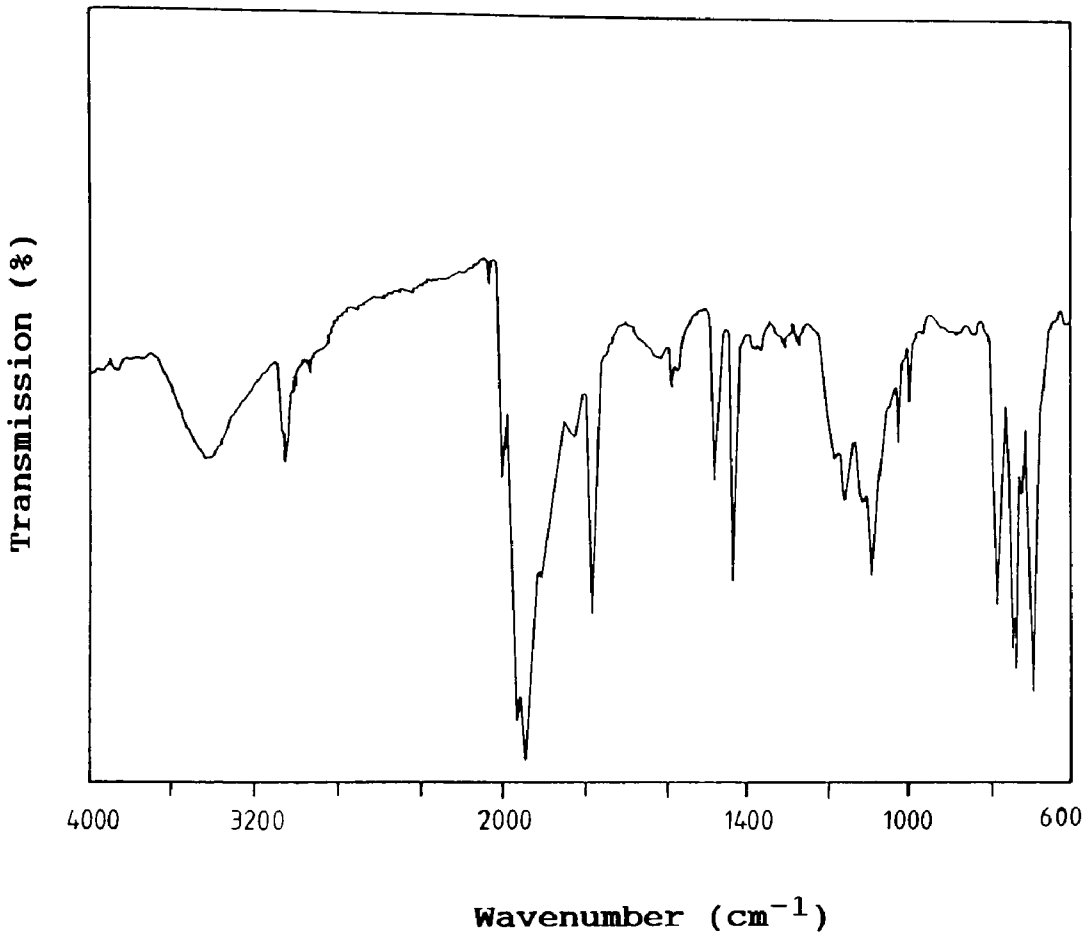


Figure 61 : IR spectrum of product of reaction 5.3.(b). (in KBr disc)

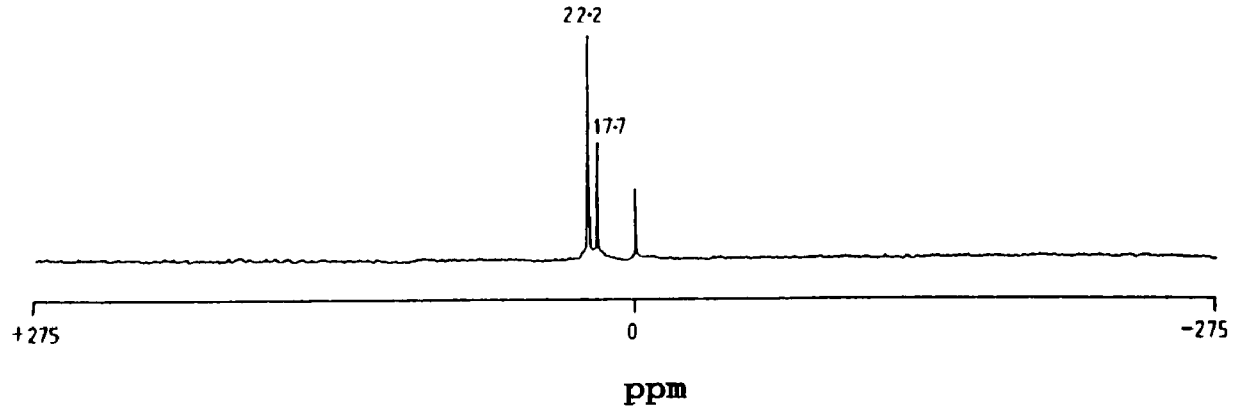


Figure 62 : ^{31}P-NMR spectrum of product of reaction 5.3.(b). (in $CDCl_3$, 85% H_3PO_4)

$[Ni(CO)_2(dppm\text{-}P)_2]$ did not rearrange rapidly to the dimer if the solution was cooled. Therefore, the reaction between $[Ni(CO)_2(dppm\text{-}P)_2]$ and $[Mo(CO)_3(C_7H_8)]$ was repeated at -50 ^0C by surrounding the reaction vessel with a mixture of liquid nitrogen and ethyl acetate as coolant. The resultant product was found as the starting material, $[Ni(CO)_2(dppm\text{-}P)_2]$.

Therefore, $[Ni(CO)_2(dppm\text{-}P)_2]$ does not react with $[Mo(CO)_3(C_7H_8)]$ but rearranges in solution to give $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$. The structure of this complex is given in figure 63.

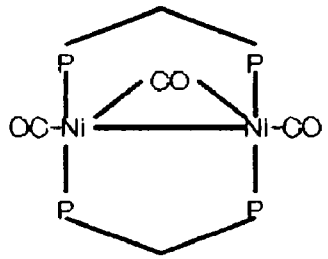


Figure 63 : Structure of $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$

The same reaction was effected using $[Mo(CO)_3(MeCN)_3]$ and gave a result as for $[Mo(CO)_3(C_7H_8)]$.

(c). Reaction of $[Ni(CO)_2(dppm\text{-}P)_2]$ with $[PdCl_2(COD)]$: Synthesis of a mixture of $[NiPdCl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ and $[PdCl_2(dppm\text{-}PP')]$

The reaction of $[Ni(CO)_2(dppm\text{-}P)_2]$ with $[PdCl_2(COD)]$ has been done at room temperature [section 5.2.(d).] and repeated at -18 ^0C and -50 ^0C. Each of these reactions

give a deep blue product which appears to be a mixture of species. The presence of a bridging carbonyl and phosphorus atoms of dppm ligands in the reaction product was confirmed by IR and ^{31}P-NMR spectroscopy. These results suggest the presence of a Ni-Pd heterobimetallic complex of the type $[NiPdCl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ analogous with a corresponding Ni-Pt heterobimetallic complex[10] $[NiPtCl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ prepared from the reaction of the same starting material, $[Ni(CO)_2(dppm\text{-}P_2]$ with $[PtCl_2(COD)]$ in CH_2Cl_2 at room temperature. A monomeric Pd(II) complex $[PdCl_2(dppm\text{-}PP')]$ and dimeric nickel complex $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ have also been identified.

The infrared spectrum of the product (KBr disc) (figure 64) gives only a sharp ν(CO) absorption band at 1786 cm^{-1} suggesting a bridging carbonyl stretching frequency. The far infrared spectrum of the product (CsI disc) gives a weak broad band at 315 cm^{-1} which may be from a terminal ν(Ni-Cl)[85] and a ν(Pd-Cl)[98] because values for both ν(Ni-Cl) and ν(Pd-Cl) appear around this area[98]. A fusion test of the reaction product gives a positive test for chlorine. Therefore, two terminal M-Cl bonds, Ni-Cl and Pd-Cl can be suggested in the reaction product by analogue with the corresponding Ni-Pt heterobimetallic complex[10] $[NiPtCl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$.

The ^{31}P-NMR spectrum of the product has been done both at room temperature and -50 ^{0}C from which a mixture of

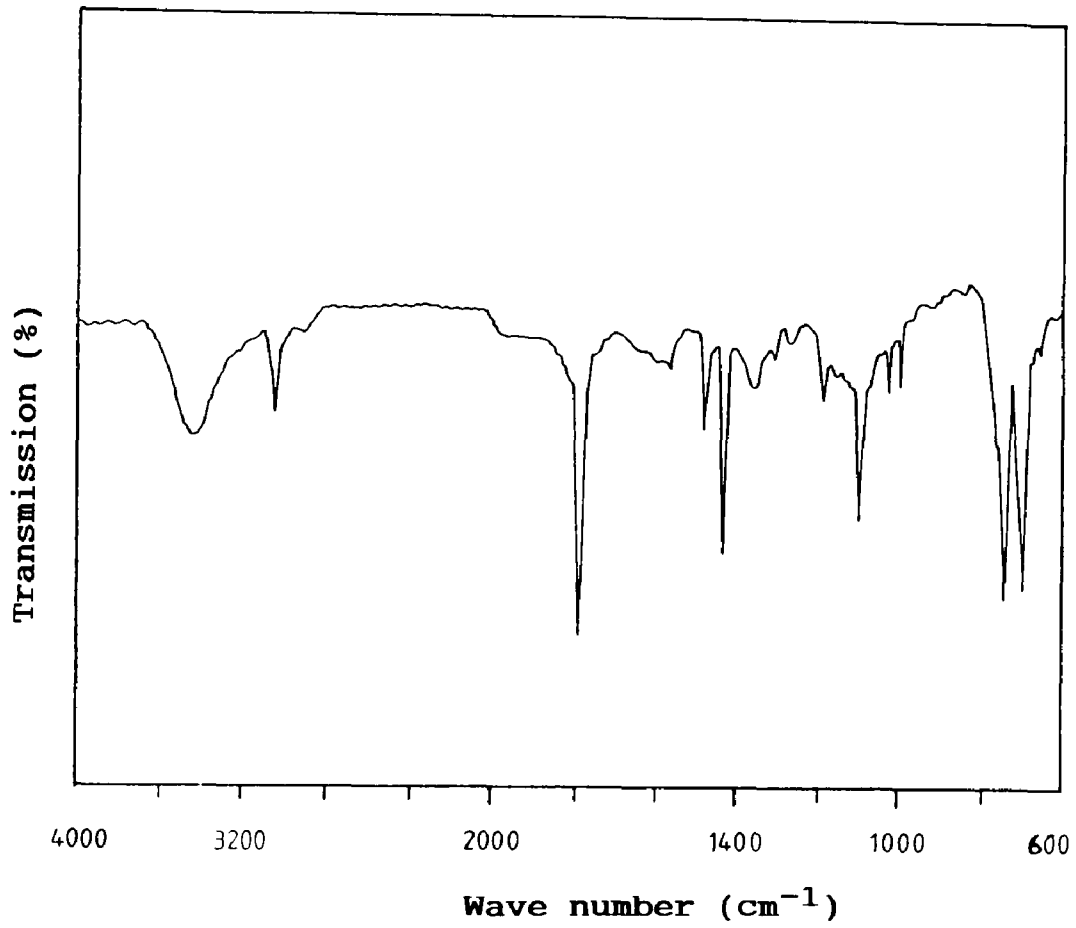


Figure 64 : IR spectrum of product of reaction 5.3.(c). (in KBr disc)

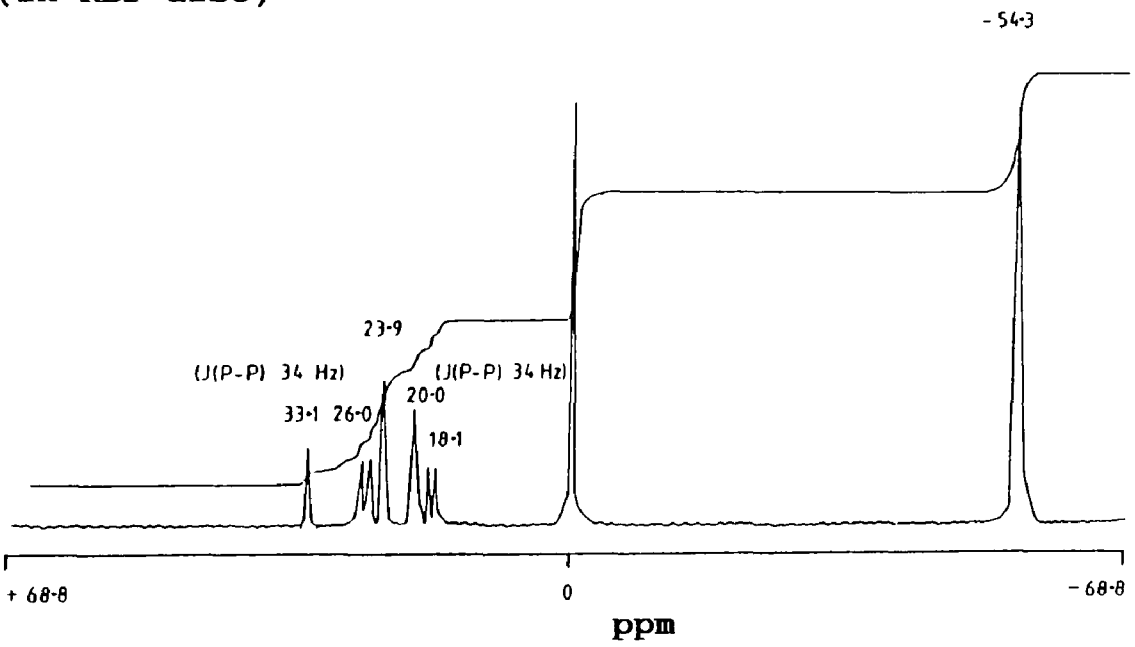


Figure 65 : ^{31}P-NMR spectrum of product of reaction 5.3.(c). (in $CDCl_3$, 85% H_3PO_4)

species including a Ni-Pd heterobimetallic complex of the type $[NiPdCl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$, a monomer $[PdCl_2(dppm\text{-}PP')]$ and a dimer $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ have been identified. At room temperature, the spectrum of the product (figure 65) shows two doublet resonances as well as some singlet resonances at δ 33.1, 23.9, 20.0 and -54.3 . The low field doublet found at δ 26.0 ($^2J(P\text{-}P)$ 34 Hz) has been assigned to two phosphorus atoms bonded to nickel[111,121] and the high field doublet observed at δ 18.1 ($^2J(P\text{-}P)$ 34 Hz) has been identified for two phosphorus atoms bonded to palladium[109,126,138]. The integration ratio of these two resonances has been found to be 1:1. A singlet resonance absorbance found in the spectrum at δ -54.3 has been identified for two phosphorus atoms of the dppm of $[PdCl_2(dppm\text{-}PP')]$[139]. The spectrum also shows three other singlet resonances at δ 33.1, 23.9 and 20.0 of which δ 33.1 could not be identified but the δ 23.9 has been identified for a dimeric nickel complex $[Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]$[9]. The singlet resonance at δ 20.0 could possibly correspond to another dppm bridged nickel dimer[9]. D. G. Holah et al.[10] reported that the Ni-Pt heterobimetallic complex $[NiPtCl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ reverts partially to $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ and $[PtCl_2(dppm\text{-}PP')]$ in CH_2Cl_2 at room temperature. Therefore, it is suggested that the Ni-Pd heterobimetallic complex formed has also reverted partially to $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ and $[PdCl_2(dppm\text{-}PP')]$. Because Holah et al.[10] have reported that the rearrangement of $[NiPtCl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$

occurs at room temperature the preparation was repeated at low temperature (-50 ^{0}C) and the ^{31}P-NMR of the product in the same solvent at -50 ^{0}C also indicated the formation of $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$. But the integration ratio of the resonances observed in the spectrum indicates a greater proportion of the heterobimetallic complex $[NiPdCl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ as compared with dimer $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ and $[PdCl_2(dppm\text{-}PP')]$ than that at room temperature.

The structure of the Ni-Pd heterobimetallic complex is suggested as in figure 67 by comparison with the corresponding Ni-Pt heterobimetallic complex[10] $[NiPtCl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$.

At room temperature, if the solution of the blue coloured product in CH_2Cl_2 or $CDCl_3$ was left for 1-2 hours it changed to yellow and the ^{31}P-NMR of this solution (figure 66) shows two singlet resonances at δ 23.4 and -54.3 which are identified[10,139] for $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ and $[PdCl_2(dppm\text{-}PP')]$ respectively.

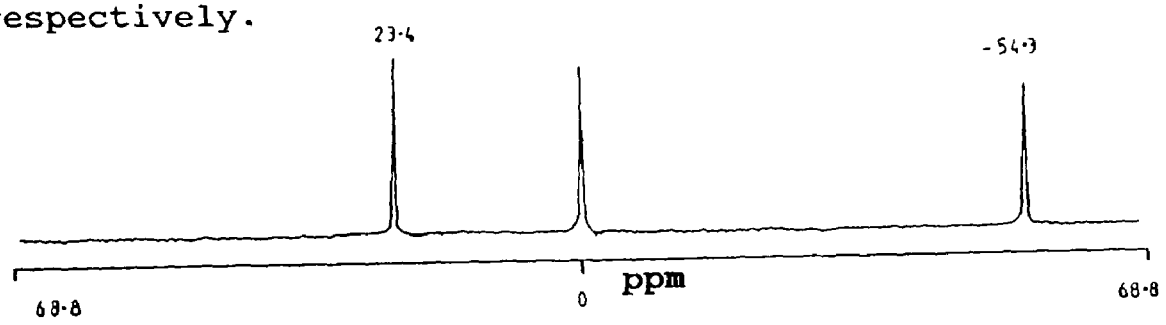


Figure 66 : ^{31}P-NMR spectrum of a mixture of $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ and $[PdCl_2(dppm\text{-}PP')]$ (in $CDCl_3$, 85% H_3PO_4)

It has been observed that the proportion of the heterobimetallic species present in the mixture depends upon the temperature at which the products are formed and it increases as room temperature < 18 ^{0}C< -50 ^{0}C. D. G. Holah et al.[10] has established the structure of a Ni-Pt heterobimetallic complex [$NiPtCl_2(\mu$-CO)(μ-dppm)$_2$] only by the determination of a crystal structure. They have mentioned that this product reverts to [$Ni_2(CO)_2(\mu$-CO)(μ-dppm)$_2$] and [$PtCl_2$(dppm-PP')] in CH_2Cl_2 at room temperature but neither published the ^{31}P-NMR spectrum of the complex nor described the process of getting the same in a pure state. This complex has been prepared here by the reported procedure[10]. IR of the product shows a bridging v(CO) at 1754 (s) cm^{-1} which agrees with the literature value for bridging v(CO)[10] in [$NiPtCl_2(\mu$-CO)(μ-dppm)$_2$]. The ^{31}P-NMR has been done at room temperature from which no resonances could be identified for [$NiPtCl_2(\mu$-CO)(μ-dppm)$_2$] because of decomposition. It has been found that the spectrum is contaminated with impurities. The spectrum shows a singlet at δ 24.7 which can be suggested[9] for [$Ni_2(CO)_2(\mu$-CO)(μ-dppm)$_2$]. Another broad resonance found around δ -22.0 can be considered for free dppm because the ^{31}P-NMR spectra of dppm shows a singlet resonance at δ -22.2 (appendix figure 10). The spectrum also shows a singlet at δ -37.0 (uncoupled P) and doublet at δ -37.0 (J(Pt-P) 2030 Hz) which is identified for [$PtCl_2$(dppm-PP')]. White coloured [$PtCl_2$(dppm-PP')] has been prepared by reacting dppm[140]

with $[K_2(PtCl_4)]$. The ^{31}P-NMR spectrum of the product exhibits a singlet at δ -37.3 (uncoupled P) and doublet at δ -37.3 (J(Pt-P) 2036 Hz). The spectrum also shows a very small singlet at δ -22.2 which is assigned to free dppm. The reported Ni-Pt heterobimetallic complex[10] $[NiPtCl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ contains one bridging carbonyl and two bridging dppm ligands between Ni and Pt, it also contains two terminal chlorine atoms bonded to both Ni and Pt and has an A-frame structure[10,141]. The reported crystal structure[10] of the Ni-Pt complex indicates a Ni-Pt bond that would give a stable electronic configuration to the complex. Hence, it can be suggested here that the Ni-Pd heterobimetallic complex synthesized here also has an A-frame structure as shown in figure 67. The structure of $[PdCl_2(dppm\text{-}PP')]$ is similar to $[NiCl_2(dppm\text{-}PP')]$ (figure 5).

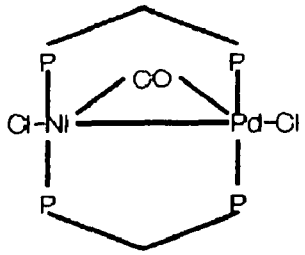


Figure 67 : Structure of $[NiPdCl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$

(d). Reaction of $[Ni(CO)(dppe\text{-}PP')(dppe\text{-}P)]$ with $[PdCl_2(COD)]$: Formation of $[NiCl_2(dppe\text{-}PP')]$

Treatment of $[Ni(CO)(dppe\text{-}PP')(dppe\text{-}P)]$ with $[PdCl_2(COD)]$ has been performed with the objective of synthesizing a heterobimetallic complex, but the

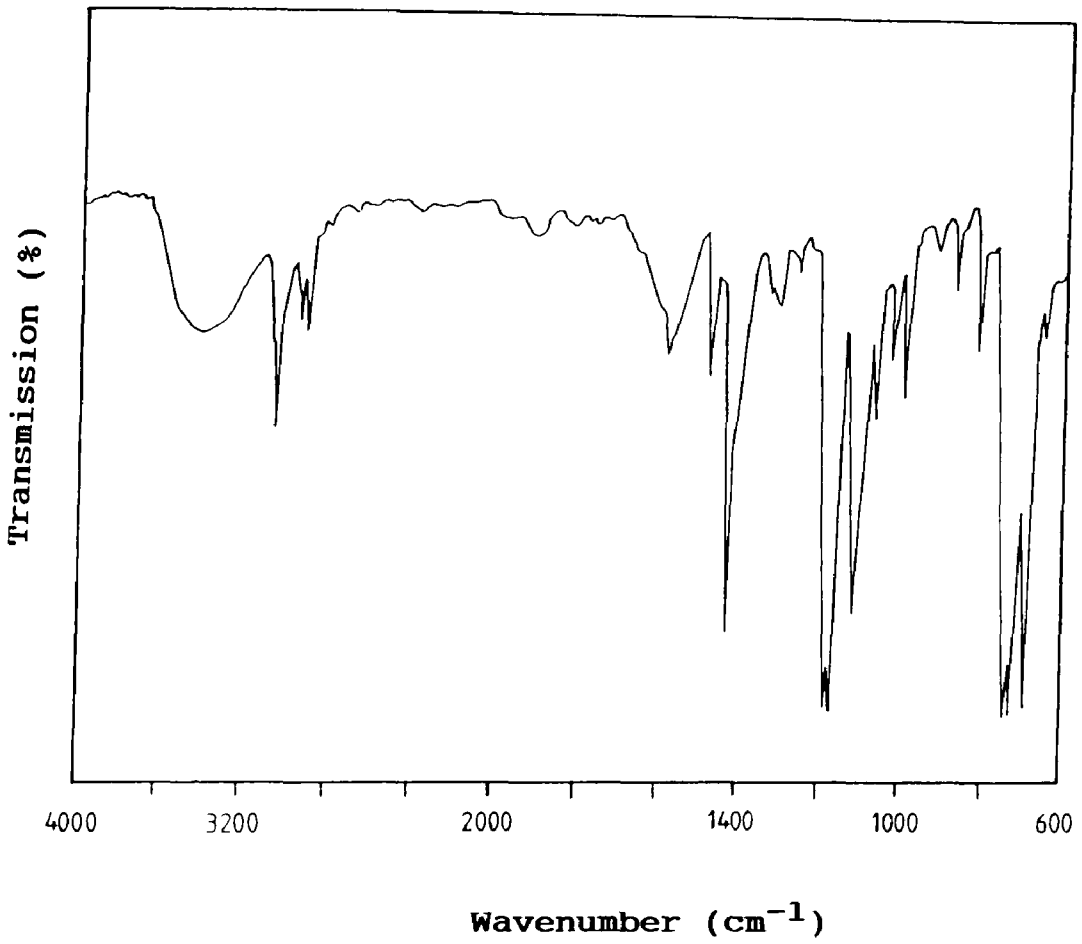


Figure 68 : IR spectrum of mixture of reaction 5.3.(d). (in KBr disc)

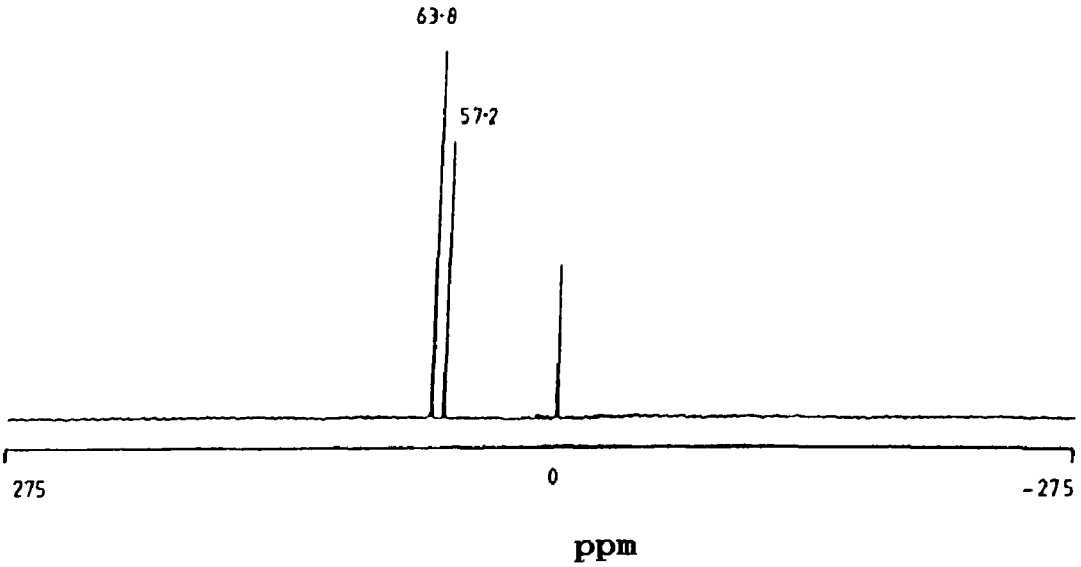


Figure 69 : ^{31}P-NMR spectrum of mixture of reaction 5.3.(d).(in $CDCl_3$, 85% H_3PO_4)

reaction gives a brown-orange product which is identified as a mixture of two species. One has been identified as $[NiCl_2(dppe\text{-}PP')]$ and the other is unidentified.

The IR of the reaction product (KBr disc) (figure 68) exhibits no $\nu(CO)$ in the carbonyl region. $\nu(C\text{-}H)$ (aromatic), $\nu(C\text{-}H)$ (aliphatic) and $\nu(P\text{-}Ph)$[86-87] have been found at 3050 (w) cm^{-1}, 2910 (w) cm^{-1} and 1434 (s) cm^{-1} respectively. The far infrared (CsI disc) shows a broad band at 328 cm^{-1} which has been identified for a terminal $\nu(Ni\text{-}Cl)$[85].

The ^{31}P-NMR spectrum of the product (figure 69) shows two very sharp singlet resonances at δ 57.2 (s) and δ 63.8 (s). The resonance found at δ 57.2 has been assigned to two phosphorus atoms of the chelating dppe ligand in the bis chloro nickel(II) complex $[NiCl_2(dppe\text{-}PP')]$ [section 4.4.(b). and 4.4.(d)]. The other singlet resonance found at δ 63.8 (s) could not be identified.

(e). Reaction of $[Ni(CO)(dppe\text{-}PP')(dppe\text{-}P)]$ with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$: Formation of a mixture of $[RhCl(CO)(dppe\text{-}PP')]$, $[RhCl(dppe\text{-}PP')_2]$ and $[Ni(dppe\text{-}PP')_2]$

Treatment of $[Ni(CO)(dppe\text{-}PP')(dppe\text{-}P)]$ with 0.5 mol equivalent of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ in dichloromethane gives

a yellow product which is identified as a mixture of species [RhCl(CO)(dppe-PP')], [RhCl(dppe-PP')$_2$] and [Ni(dppe-PP')$_2$].

The infrared spectrum of the product (KBr disc) (figure 70) exhibits no $\bar{\nu}$(CO) (bridging) in the bridging carbonyl region, but it gives a single band at 2010 (s) cm^{-1} which is assigned to a terminal $\bar{\nu}$(CO). A. R. Sanger[112] has reported that the IR of the monomer complex [RhCl(CO)(dppe-PP')] shows $\bar{\nu}$(CO) at 2010 cm^{-1}. The Far infrared spectrum of the prepared product (CsI disc) shows a broad band at 300 cm^{-1} which may be due to terminal $\bar{\nu}$(Rh-Cl)[15].

The ^{31}P-NMR spectrum of the product (figure 71) is consisted of two doublets of doublets at δ 69.2 and δ 47.5 reflecting the difference between phosphorus atoms trans to Cl and to CO (^{3}J(P-P) 34 Hz)[16] as well as some other resonances. The signal at δ 69.2 (dd) has been assigned for the phosphorus atom of the dppe ligand bonded to rhodium and trans to Cl[16,112], and that at δ 47.5 (dd) is due to the phosphorus atom of the ligand bonded to rhodium and trans to CO[16,112]. Coupling constant values for J(Rh-P) found are 160 and 127 Hz. These values are in agreement with those found for the complex [RhCl(CO)(dppe-PP')] reported by A. R. Sanger et al.[16,112]. The ^{31}P-NMR also exhibits a doublet at δ 56.2 (J(Rh-P) 132 Hz) which has been identified as representing the equivalent phosphorus atoms[16] in

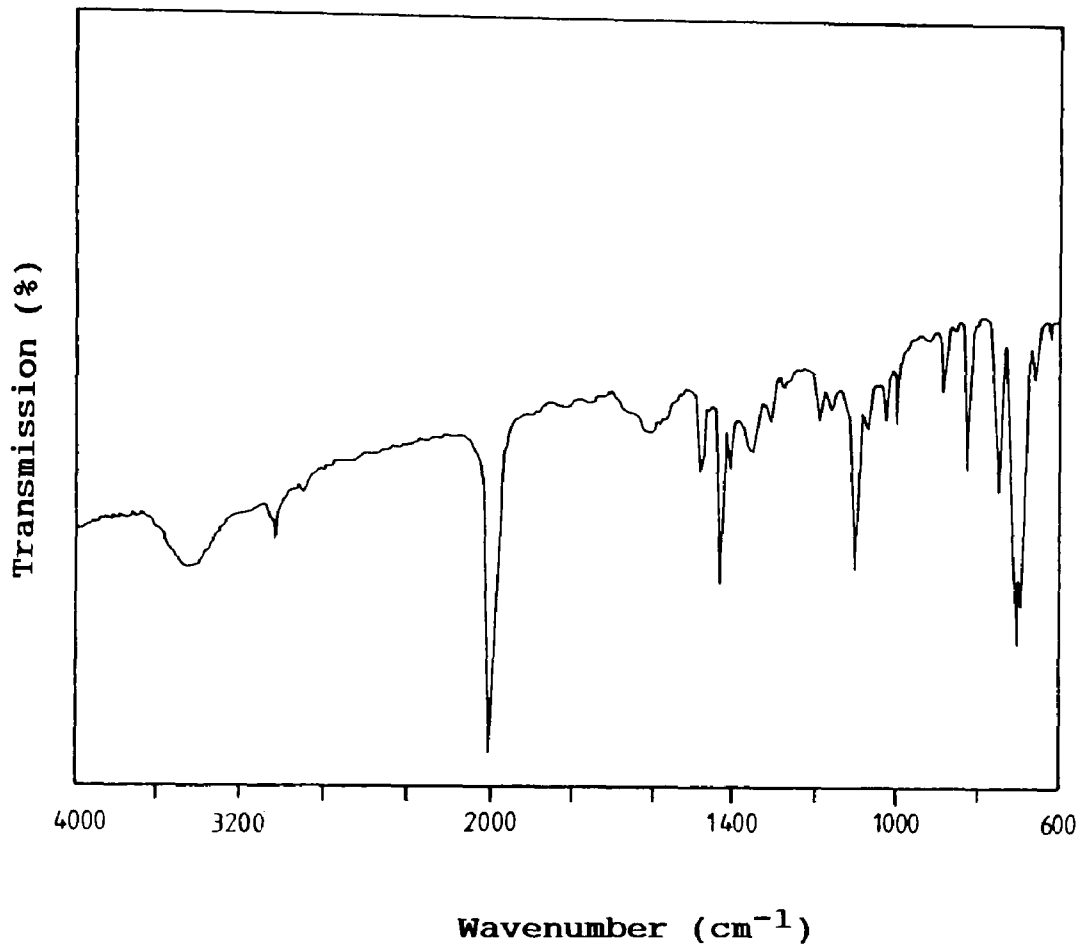


Figure 70 : IR spectrum of mixture of reaction 5.3.(e). (in KBr disc)

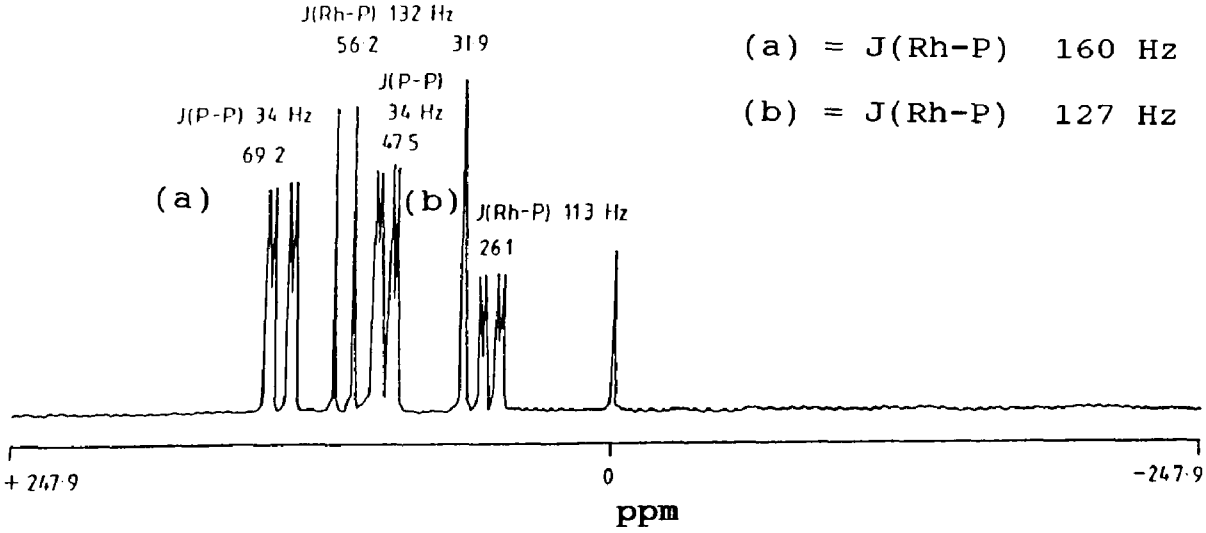


Figure 71 : ^{31}P-NMR spectrum of mixture of reaction 5.3.(e). (in $CDCl_3$, 85% H_3PO_4)

[RhCl(dppe-PP')$_2$]. The singlet resonance observed at δ 31.9 is considered for [Ni(dppe-PP')$_2$] [section 4.4.(e).]. The spectrum also shows a doublet of doublets resonance at δ 26.1 (J(Rh-P) 113 Hz)) which because of the pattern of coupling, is probably another Rh-dppe species, but can not be identified. The complex [Rh$_2$(μ-Cl)$_2$(CO)$_4$] reacts with the appropriate amount of dppe (one equivalent of dppe per Rh atom) in benzene to afford the neutral monomer complex[16,112] [RhCl(CO)(dppe-PP')].

Therefore, treatment of 0.5 mol equivalent of [Rh$_2$(μ-Cl)$_2$(CO)$_4$] with [Ni(CO)(dppe-PP')(dppe-P)] does not give a heterobimetallic complex but it produces a monomeric square planar rhodium complex [RhCl(CO)(dppe-PP')] with a mixture of [RhCl(dppe-PP')$_2$] and [Ni(dppe-PP')$_2$]. The structures of [RhCl(CO)(dppe-PP')] and [RhCl(dppe-PP')$_2$] are therefore given as in figure 72.

(a) (b)

Figure 72 : Structures of (a) [RhCl(CO)(dppe-PP')] (b) [RhCl(dppe-PP')$_2$]

(f). Reaction of [Ni(CO)(dppe-PP')(dppe-P)] with [Mo(CO)$_3$(C_7H_8)]: An Attempt to Synthesize a Ni-Mo Heterobimetallic Complex containing Bridging dppe Ligand

This reaction has been done at both room and low temperature (-18 ^{0}C), but in each case the reaction does not give a bimetallic complex. A light brown coloured product has been collected by reprecipitation of the reaction mixture which is characterized as [Ni(dppe-PP')$_2$].

The IR of the product (KBr disc) shows a $\bar{\nu}$(CO) at 1922 cm^{-1} with an weak $\bar{\nu}$(CO) at 1972 cm^{-1} which may be for unreacted starting materials, because the IR (KBr disc) [Mo(CO)$_3$(C_7H_8)] gives $\bar{\nu}$(CO) at 1972 (s), 1911 (s) and 1852 (s) cm^{-1}.

The ^{31}P-NMR of the product shows the same result in both cases. It gives a singlet resonance at δ 32.7 (figure 73) which has already been assigned to four equivalent phosphorus atoms of the dppe ligands bonded to nickel in [Ni(dppe-PP')$_2$] [section 4.3]. [Ni(dppe-PP')$_2$] has been prepared [section 4.3] and it has been found that the ^{31}P-NMR spectrum of this (appendix figure 5) gives a sharp singlet resonance at δ 32.4. So, here, the reaction does not give any bimetallic product, but a product [Ni(dppe-PP')$_2$] has been formed. This could probably due to the excellent chelating nature of dppe to form a stable five membered

monomer complex[35]. If the reaction is stopped, 10 minutes after addition of $[Mo(CO)_3(C_7H_8)]$ to $[Ni(CO)(dppe\text{-}PP')(dppe\text{-}P)]$ the IR of the reaction mixture (solution) (KBr disc) shows both terminal ($\tilde{\nu}$(CO) at 2067, 1977, 1899 cm^{-1}) and bridging ($\tilde{\nu}$(CO) at 1745 cm^{-1}) carbonyl groups. This result may indicate the initial formation of a bimetallic complex which rapidly rearranges in solution.

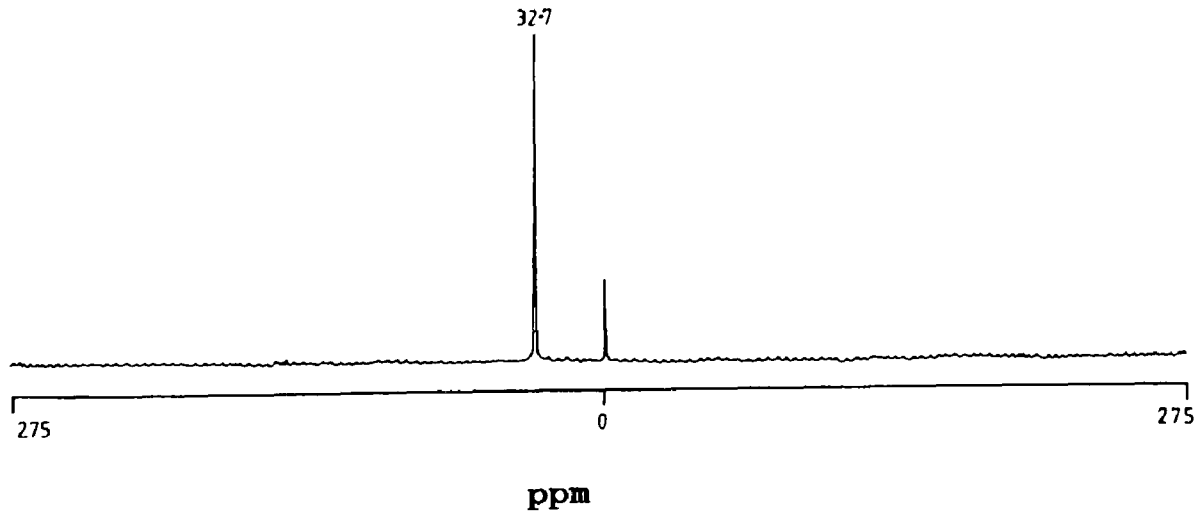


Figure 73 : ^{31}P-NMR spectrum of $[Ni(dppe\text{-}PP')_2]$ from reaction 5.3.(f). (in $CDCl_3$, 85% H_3PO_4)

(g). Reaction of $[Ni(CO)_2(dppm\text{-}P)_2]$ with $[W(CO)_4(MeCN)_2]$: An attempt to synthesize a Ni-W Heterobimetallic Complex

Attempts to synthesize a Ni-W heterobimetallic complex resulted in the rearrangement of $[Ni(CO)_2(dppm\text{-}P)_2]$ giving the dimer $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$. The IR of the product (KBr disc) shows a broad band for $\tilde{\nu}$(CO)

(terminal) between 2000-1940 cm^{-1} and $\tilde{\nu}$(CO) (bridging) at 1780 (s) cm^{-1} which are in agreement with the literature $\tilde{\nu}$(CO) values[9] of $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$. However, no heterobimetallic complex was formed in the reaction of the complex $[Ni(CO)_2(dppm\text{-}P)_2]$ and $[W(CO)_4(MeCN)_2]$ as for $[Mo(CO)_3(MeCN)_3]$.

(h). Reaction of $[Ni(CO)_2(dppm\text{-}P)_2]$ with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$: Preparation of a mixture of *trans*-$[RhCl(CO)(\mu\text{-}dppm)]_2$ and $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$

Reaction of $[Ni(CO)_2(dppm\text{-}P)_2]$ with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ gave an orange coloured product. Part of the the product was soluble in organic solvents. The IR of the product (KBr disc) (figure 74) shows a sharp $\tilde{\nu}$(CO) (terminal) band at 1968 cm^{-1} and a bridging $\tilde{\nu}$(CO) at 1760 cm^{-1}. The literature shows that the dinuclear complex[15,16,112] *trans*-$[RhCl(CO)(\mu\text{-}dppm)]_2$ has been characterized from the reaction of dppm and $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ and it is insoluble[142] in CH_2Cl_2. $\tilde{\nu}$(CO)[15,16,112] of this complex has been reported at 1968 (s) cm^{-1}. Again, $\tilde{\nu}$(CO) (bridging)[114] of $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ is reported at 1745 cm^{-1}. So, infrared suggests that the product formed here could possibly be a mixture of components containing *trans*-$[[RhCl(CO)(\mu\text{-}dppm)]_2$ and $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$. The product is partially soluble in $CDCl_3$. Because of its limited solubility, difficulty was encountered in obtaining its ^{31}P-NMR spectrum. Only a doublet at δ 19.7 (J(Rh-P) 116 Hz)

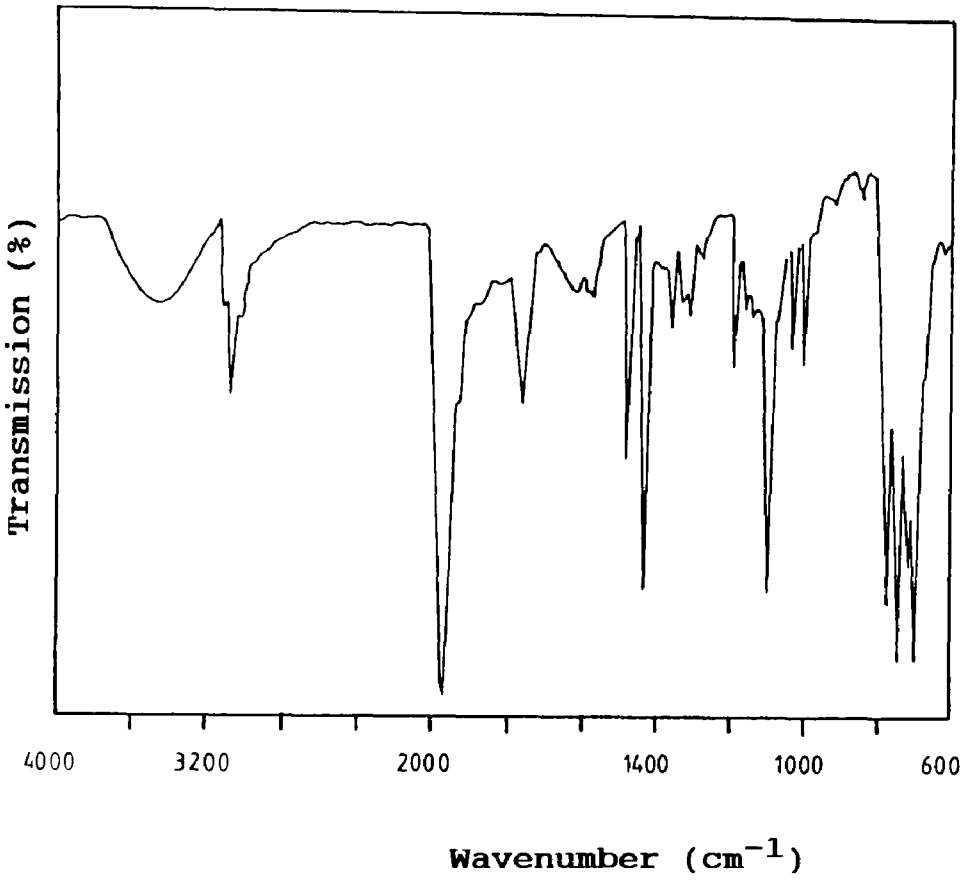


Figure 74 : IR spectrum of mixture of reaction 5.3.(h). (in KBr disc)

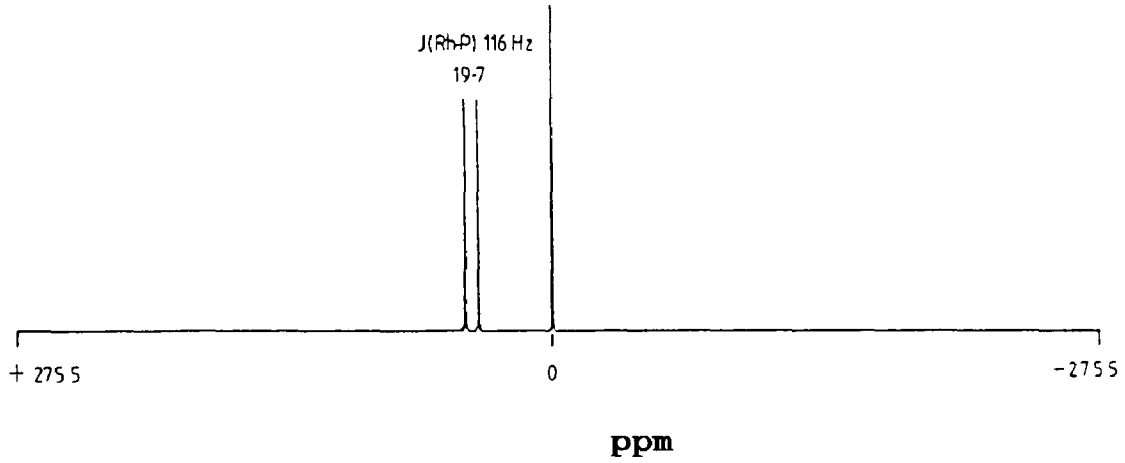
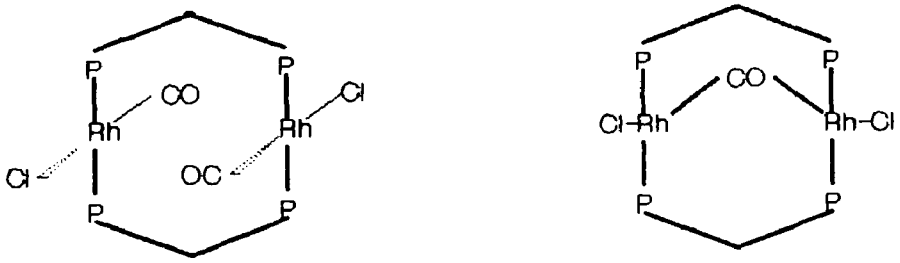


Figure 75 : ^{31}P-NMR spectrum of mixture of reaction 5.3.(h). (in $CDCl_3$, 85% H_3PO_4)

(figure 75) has been observed which may be compared with the ^{31}P-NMR spectrum of $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ reported[114] at δ 19.7 (d) ((J(Rh-P) 115.9 Hz). So, δ 19.7 (116 Hz) found could possibly be for $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ formed in the present reaction as one component. Since *trans*-$[RhCl(CO)(\mu\text{-}dppm)]_2$ is not soluble[142] in $CDCl_3$ no resonances have been found for this complex although the infrared suggests it may have been formed.

Therefore, it can only be suggested that *trans*-$[RhCl(CO)(\mu\text{-}dppm)]_2$ and $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ may be in the product of this reaction. The structures of these complexes are given in figure 76.



(a) (b)

Figure 76 : Structures of (a). *trans*-$[RhCl(CO)(\mu\text{-}dppm)]_2$ (b). $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$

5.4. CONCLUSIONS

Difficulty was encountered in the synthesis of heterobimetallic complexes using $[Ni(CO)_2(dppm\text{-}P)_2]$ and [Ni(CO)(dppe-PP')(dppe-P)]. The preparation of heterobimetallic species was eventually not as simple as outlined by D. G. Holah et al.[10] where they reported that $[Ni(CO)_2(dppm\text{-}P)_2]$ had potential in the synthesis of heterobimetallic complexes with $[PtCl_2(COD)]$, $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$, $[Mo(CO)_5THF]$ and $[NiCl_2.6H_2O]$. At room temperature $[Ni(CO)_2(dppm\text{-}P)_2]$ rearranges to the dimer[9] $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ in solution unless it is cooled or an excess of dppm is present in the solution. This result was observed with its reactions with $[Mo(CO)_3(C_7H_8)]$, $[Mo(CO)_3(MeCN)_3]$ and $[W(CO)_4(MeCN)_2]$. At lower temperatures (-18 ^{0}C and -50 ^{0}C) $[Ni(CO)_2(dppm\text{-}P)_2]$ did not rearrange in solution but it did not react with the above mentioned compounds and remained intact. A Ni-Pd heterobimetallic complex $[NiPdCl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ was identified with some impurities from the reaction of $[Ni(CO)_2(dppm\text{-}P)_2]$ and $[PdCl_2(COD)]$ which rearranged rapidly in solution[10] at room temperature. Therefore, the Ni-Pd species could not be separated from the mixtures formed by column chromatography or by making crystals at room temperature. The product is more stable at lower temperatures in solution. Reaction of [Ni(CO)(dppe-PP')(dppe-P)] with $[PdCl_2(COD)]$ produced a Ni(II) monomer $[NiCl_2(dppe\text{-}PP')]$ and with

$[Rh(\mu\text{-}Cl)_2(CO)_4]$ it gave a mixture of monomer complexes containing chelating dppe $[RhCl(CO)(dppe\text{-}PP')]$, $[RhCl_2(dppe\text{-}PP')]$ and $[Ni(dppe\text{-}PP')_2]$. No bimetallic complexes were obtained from any of these reactions. This is probably due to the excellent chelating nature of dppe leading to the formation of monomer complexes[35] with stable five membered rings. It has been observed that the dicarbonyl species $[Ni(CO)_2(dppm\text{-}P)_2]$ has more potential than the monocarbonyl species $[Ni(CO)(dppe\text{-}PP')(dppe\text{-}P)]$ in the synthesis of heterobimetallic complexes.

SECTION 6

SUGGESTIONS FOR FURTHER WORK

SUGGESTIONS FOR FURTHER WORK

Reactions of zerovalent nickel-CO-phosphine complexes [Ni(CO)(dppe-PP')(dppe-P)] and [$Ni(CO)_2$(dppm-P)$_2$] with alkyl, aryl, acyl and aroyl halides produce no organometallic derivatives. Reasons for the instability of these species are discussed in [section 4.1. and 4.5]. The first step of the suggested mechanism of decomposition involves loss of CO. With alkyl and aryl halides [Ni(CO)(dppe-PP')(dppe-P)] produces loss of CO and the formation of Ni(O) complex [Ni(dppe-PP')$_2$], probably due to the excellent chelating nature of dppe. These reactions could be further studied under an atmosphere of CO in an attempt to produce different reaction products.

Reactions of Air with [$Ni(CO)_2$(dppe-PP')(dppe-P)] and [$Ni(CO)_2$(dppm-P)$_2$] formed [Ni(dppe-PP')$_2$] and mixture of the monoxide and dioxides of dppm respectively at room temperature, not giving an adduct[70] of the type [NiO_2L_2] (L_2 = chelate or L = monodendate dppe, dppm). [$NiO_2(PPh_3)_2$] obtained from the reaction of [$Ni(PPh_3)_4$] with air is stable in solution below -35 ^{0}C and decomposes above -35 ^{0}C to give oxides of triphenylphosphine[70]. Most probably the adduct, if formed in these reactions, decomposed[70] at room temperature. If these reactions could be performed at a lower temperature then the adduct of the type [NiO_2L_2] might also be obtained. Therefore, the reactions of air

with $[Ni(CO)_2(dppe\text{-}PP')(dppe\text{-}P)]$ and $[Ni(CO)_2(dppm\text{-}P)_2]$ could be further studied at low temperatures in an attempt to identify the $[NiO_2L_2]$ species.

The catalytic potential of the Ni-Pt complex could be studied. For example, the complexes $[Rh_2(CO)_2(\mu\text{-}dppm)_2]$ and $[Pd_2Cl_2(\mu\text{-}dppm)_2]$ act as catalysts for hydrogenation of ethyne to ethene and cyclooligomerization of alkynes respectively[2-3]. Similarly, bimetallic complexes $[Rh_2(CO)_2(\mu\text{-}S)(\mu\text{-}dppm)_2]$, $[Ir_2(CO)_2(\mu\text{-}S)(\mu\text{-}dppm)_2]$ and $[Ir_2H_2(CO)_2(\mu\text{-}S)(\mu\text{-}dppm)_2]$ act as catalysts for hydrogenation of ethyne to ethene[4]. The heterobimetallic species Ni-Pt having the different properties of two distinct metals could display a reactivity in this area.

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APPENDICES

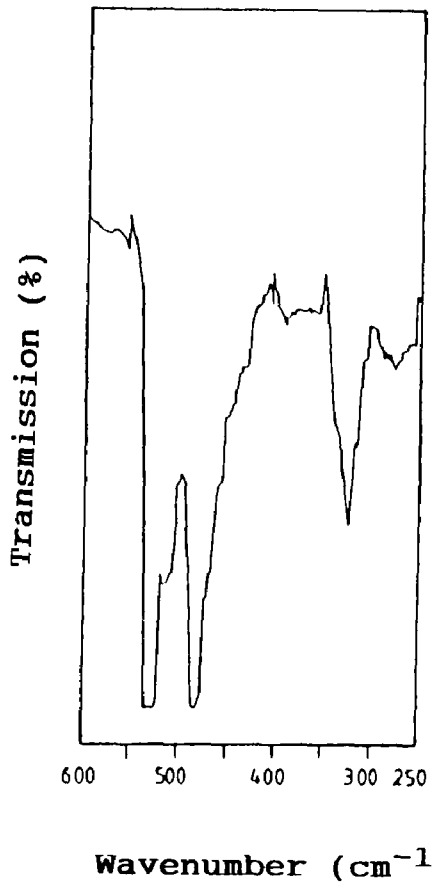


Figure 1 : Far IR spectrum of [$NiCl_2$(dppe-PP')] (in CsI)

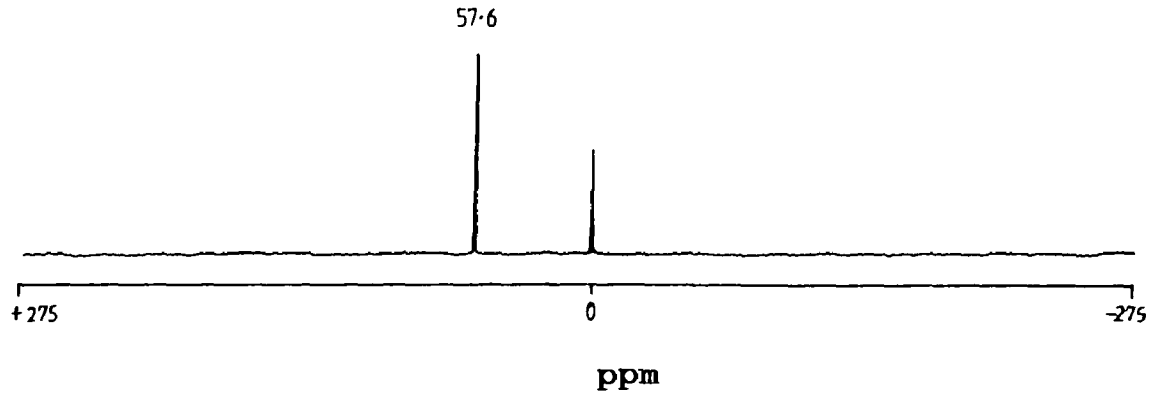


Figure 2 : ^{31}P-NMR spectrum of [$NiCl_2$(dppe-PP')] (in $CDCl_3$, 85% H_3PO_4)

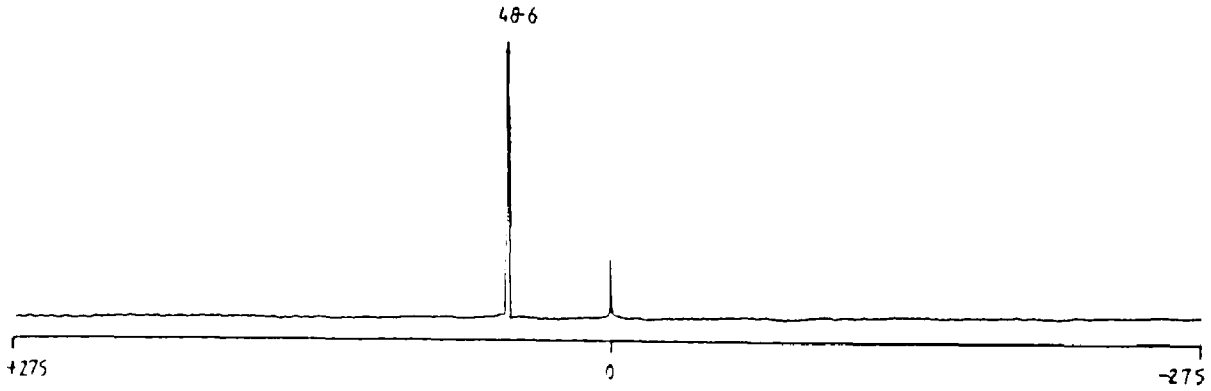


Figure 3 : ^{31}P-NMR spectrum of [NiI_2(dppe-PP')$_2$] (in $CDCl_3$, 85% H_3PO_4)

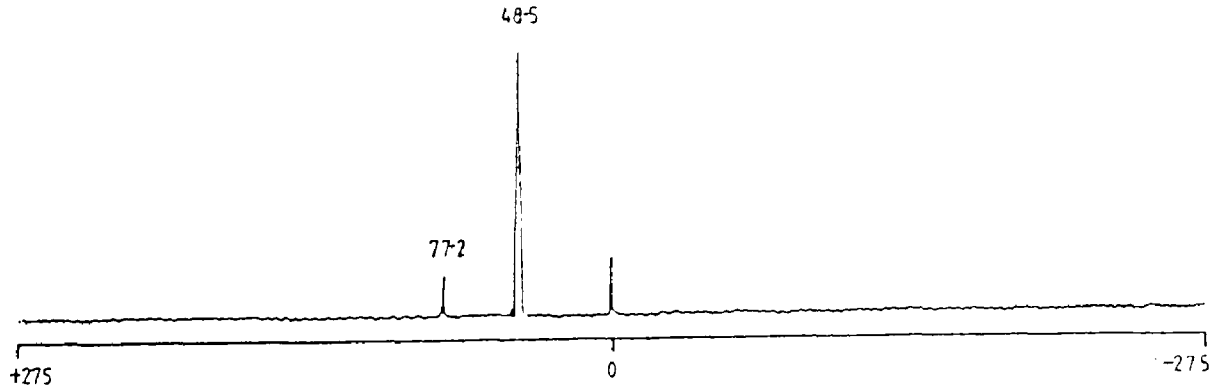


Figure 4 : ^{31}P-NMR spectrum of a mixture product of [NiI_2(dppe-PP')] and [NiI_2(dppe-PP')$_2$] (in $CDCl_3$, 85% H_3PO_4)

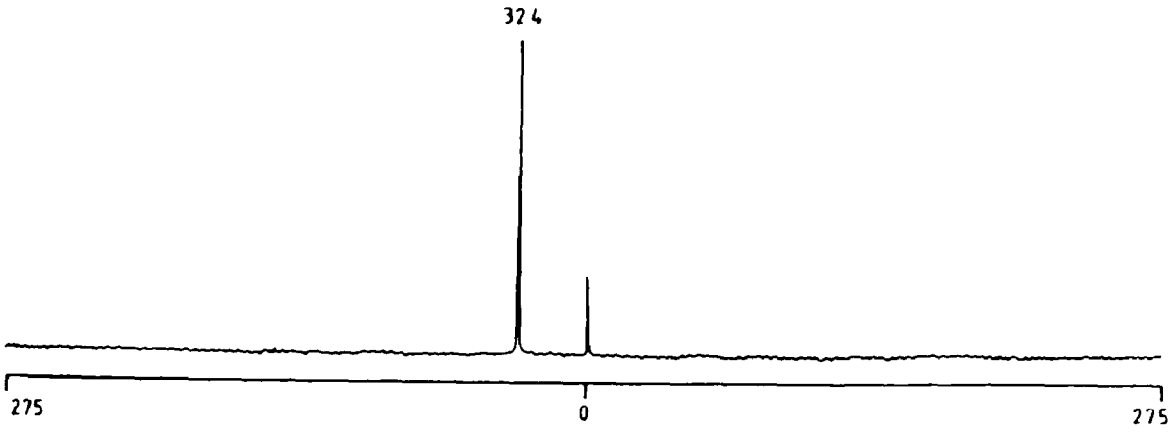


Figure 5 : ^{31}P-NMR spectrum of [Ni(dppe-PP')$_2$] (in $CDCl_3$, 85% H_3PO_4)

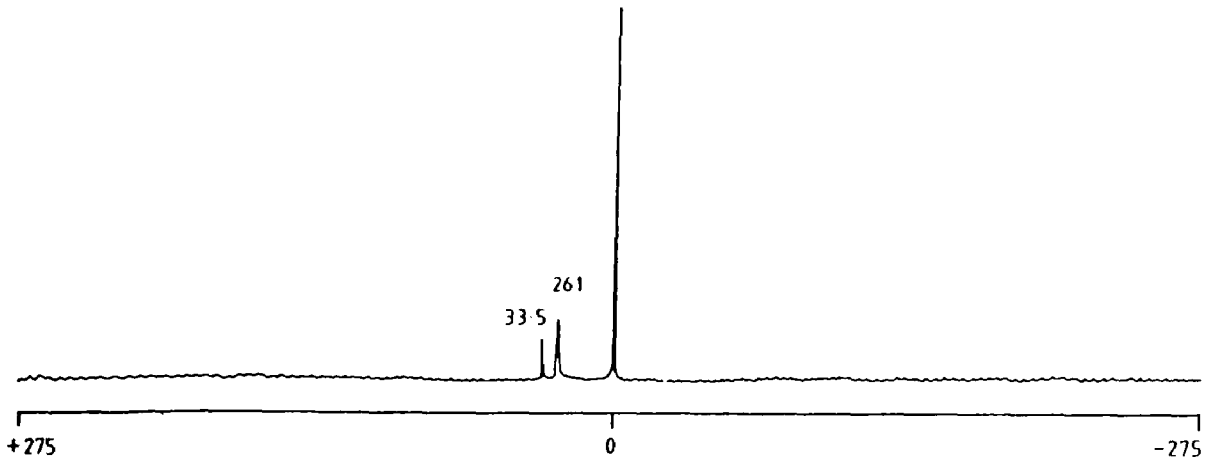


Figure 6 : ^{31}P-NMR spectrum of [NiI_2(dppm-P)] (impure) (in $CDCl_3$,85% H_3PO_4)

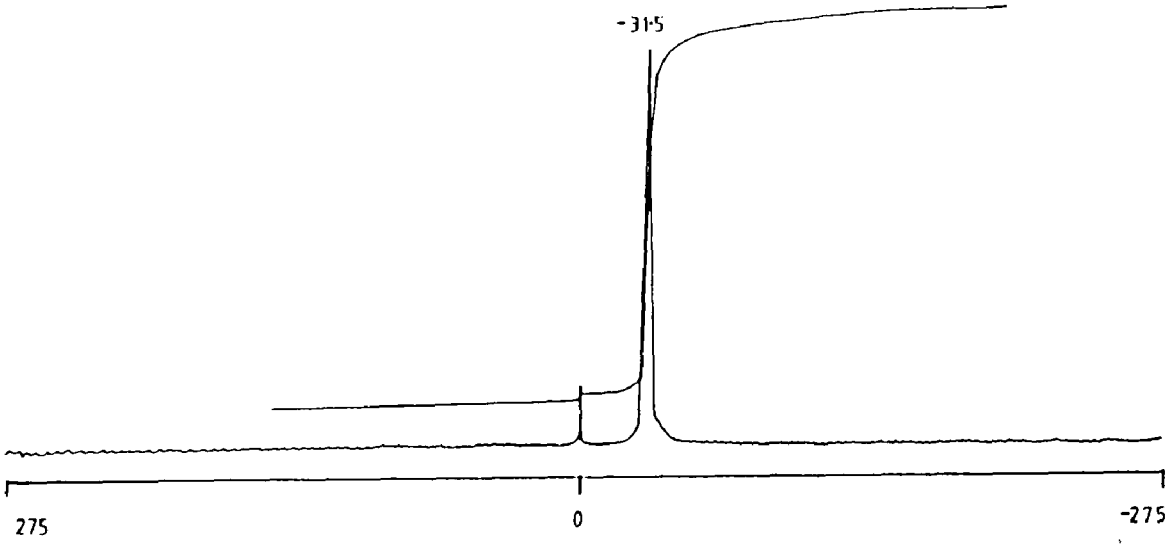


Figure 7 : ^{31}P-NMR spectrum of [NiI_2(dppm-P)$_2$] (in $CDCl_3$, 85% H_3PO_4)

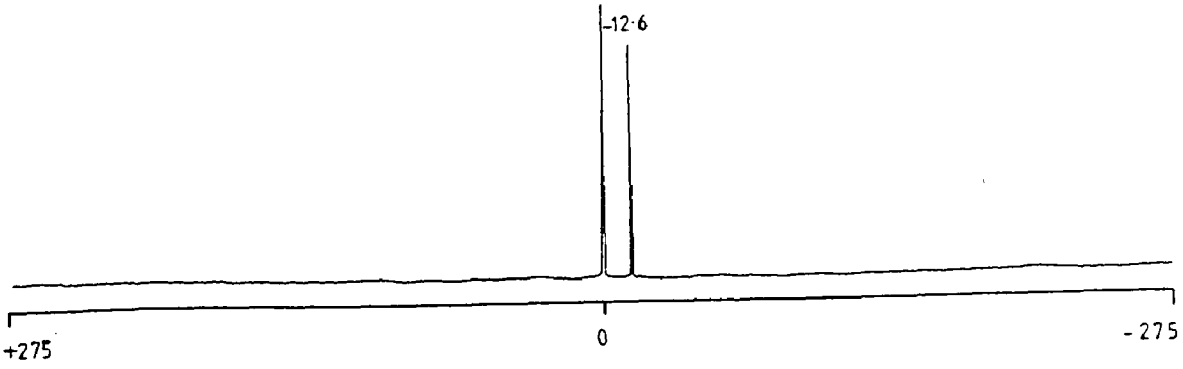


Figure 8 : ^{31}P-NMR spectrum of dppe (in $CDCl_3$, 85% H_3PO_4)

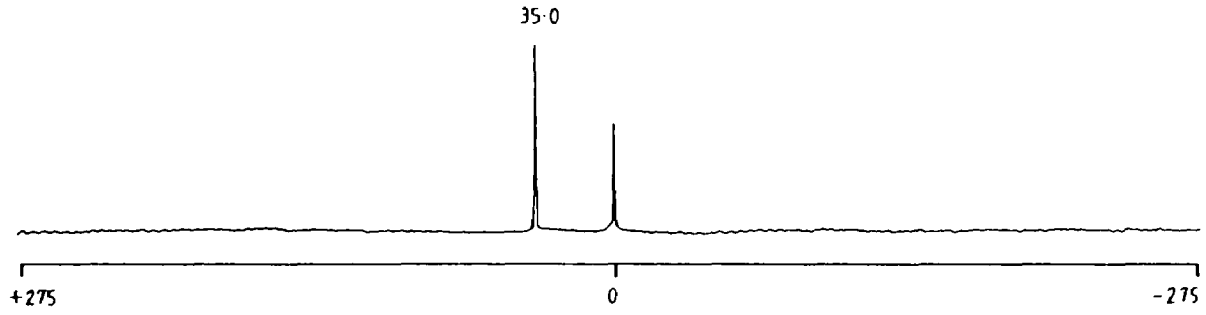


Figure 9 : ^{31}P-NMR spectrum of $[Ph_2P(O)(CH_2)_2P(O)Ph_2]$ (in $CDCl_3$, 85% H_3PO_4)

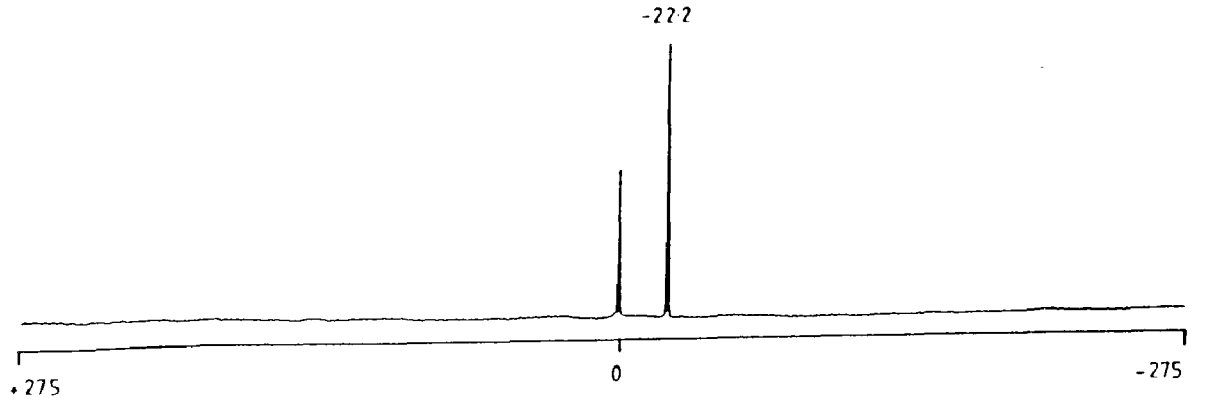


Figure 10 : ^{31}P-NMR spectrum of dppm (in $CDCl_3$, 85% H_3PO_4)

Figure 11

ν(CO) of some Ni(O)-Carbonyl-Phosphine Complexes

COMPLEXES	COLOUR	ν(CO), cm^{-1}	REFERENCE
$[Ni(CO)_3PPh_3]$	White	2063, 1987	37
$[Ni(CO)_2(dppe\text{-}PP')]$	White	1997, 1936	37
$[Ni(CO)_2(PPh_3)_2]$	Cream	1994, 1993	37
$[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$	Yellow	2000, 1972 1955, 1940 1790	9
$[Ni(CO)_2(dppm\text{-}P)_2]$	White	1986, 1926	10
$[Ni(CO)(dppe\text{-}PP')(dppe\text{-}P)]$	Yellow	1911	10

Figure 12

Far infrared spectra of some Complexes

COMPLEXES	ν(Ni-X), cm^{-1}	REFERENCE
$[NiCl_2(dppe\text{-}PP')]$	329, 341	98
$[NiCl_2(dppm\text{-}PP')]$	313	85
$[NiI_2(dppm\text{-}P)_2]$	210	85
$[NiI_2(dppe\text{-}PP')]$	216	85

Figure 13

ν(Ni-H) and High Field ^{1}H-NMR of some Nickel Hydride Complexes

COMPLEXES	ν(Ni-H), cm^{-1}	^{1}H-NMR, ppm	REF.
$[NiH(dppe\text{-}PP')_2]AlCl_4$	1950,1949,1916	- 12.95	76
$[NiH(dppe\text{-}PP')_2]BF_4$	1950	- 13.01	76
$[NiH(dppe\text{-}PP')_2]HCl_2$	1934	- 13.02	76
$[NiH\{P(OEt)_3\}_4]+$	----	- 14.30 - 14.50	75

Figure 14[114]

Spectral Data for some Rhodium dinuclear Complexes

COMPLEXES	ν(CO)[a] cm^{-1}	^{31}P-NMR[b] ppm
$[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$	1745(s)	19.7 (115.9 Hz)
$[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(\mu\text{-}dppm)_2][Cl]$	2004(m) 1960(s) 1868(m)	29.8 (94.0 Hz)

a = infrared spectra run as Nujol mulls on KBr plate

b = ^{31}P-NMR chemical shifts are relative to H_3PO_4

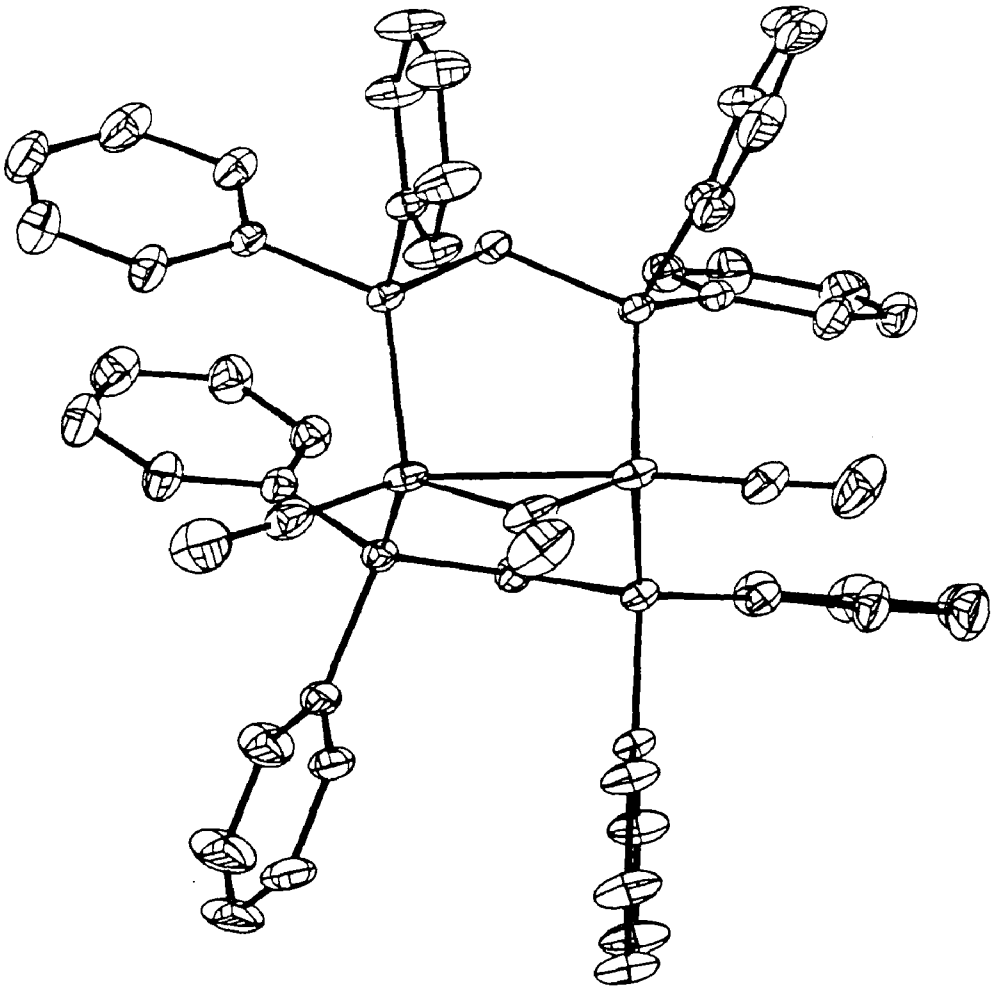
Figure 15

Crystal data and details of data collection and refinement for $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$

Formula	$[Ni_2(CO)_3(CH_2(PPh_2)_2)_2]$
M.W.	970.21
Crystal system	Monoclinic
$a/\AA$	21.236(4)
$b/\AA$	14.895(3)
$c/\AA$	15.270(5)
$\alpha/^\circ$	90
$\beta/^\circ$	100.41(1)
$\gamma/^\circ$	90
$V/\AA^3$	4750.48
θ range for cell/$^\circ$	2.5-25
Space group	$C2/c$
Z	4
D_c/gcm^{-3}	1.356
$F(000)$	2008
μ(Mo-Kα)/cm^{-1}	9.69
T/K	298
Crystal size/mm^3	0.25x0.25x0.08
θ range for data/$^\circ$	1.9-25.3
h_{min}, h_{max}	-23,23
k_{min}, k_{max}	-17,17
l_{min}, l_{max}	-9,17
Total data measured	7371
Total unique	5632
R_{int}	0.0435
Total observed	2335
Significance test	$Fo>3\sigma(Fo)$
Absorption correction factors, min, max	0.719,0.858
No. of parameters	282
ρ_{min}, $\rho_{max}/e\AA^{-3}$	-0.41,+0.98
$(\Delta/\sigma)_{max}$	0.002
Weighting scheme	unit weight
R	0.0387
wR	0.0398

Notes:
(1) Treatment of H-atoms: The two methylene H's [H(31) and H(32)] located from difference map and the calculated H's on the phenyl rings were allowed to ride on their parents [C-H=0.96Å], a common Uiso being refined for all.
(2) Structure solved by (direct methods) SHELX-S (G.M. Sheldrick, Univ. of Gottingen,1986) and refined by (least-squares) SHELX-80 (G.M. Sheldrick, Univ. of Gottingen,1980); Empirical absorption correction by DIFABS (N. Walker and D. Stuart, *Acta Cryst.*,1983,A39,158-166) adapted for FAST geometry by A. Karaulov, Univ. of Cardiff,1990); Figures drawn by SNOOPI (K. Davies, Univ. of Oxford,1983).
(3) All calculations made on a T800 transputer hosted by an IBM/AT personal computer
(4) Neutral atom scattering factors from

ALONG BO ZROT 20 XROT -20 YROT 185



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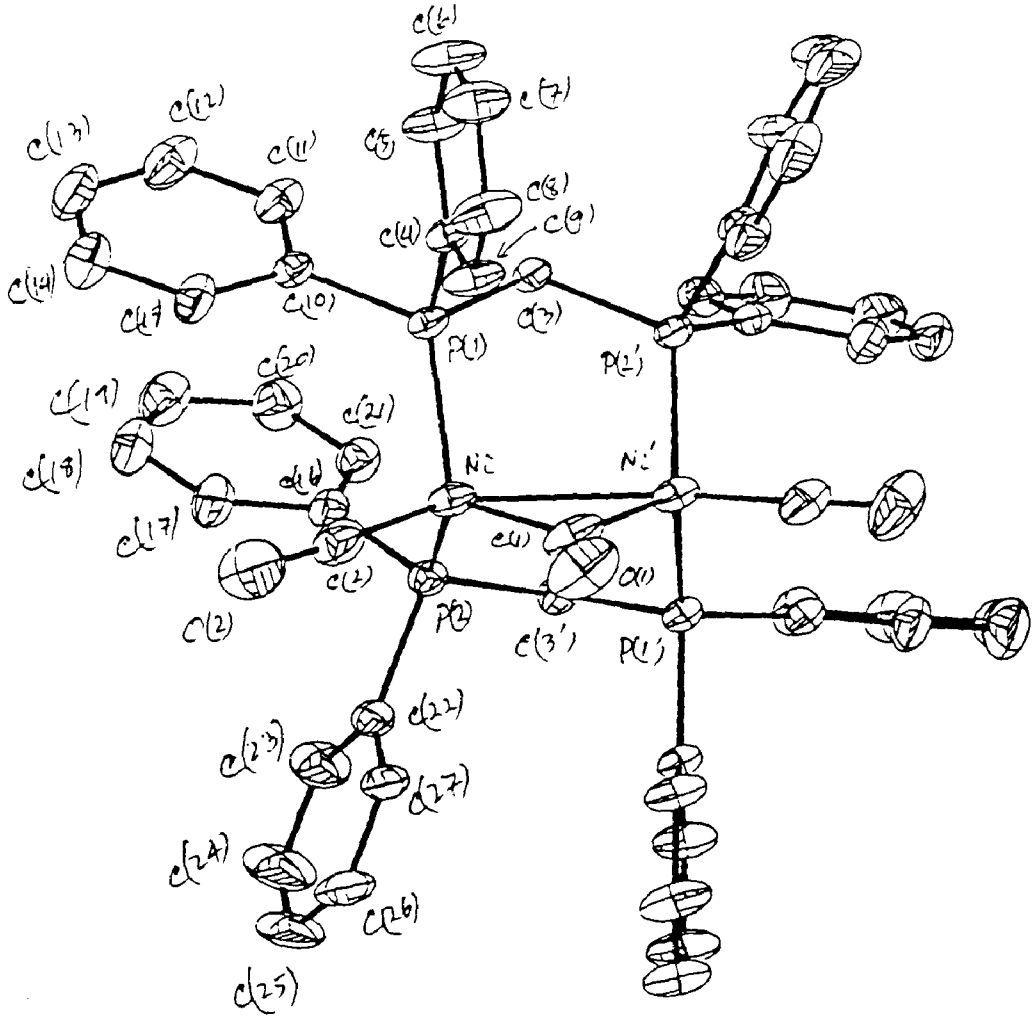

Table

Bond lengths (A) and angles (deg.) for [Ni2(CO)3{CH2(PPh2)2}2]

Ni-Ni(a)*	2.619(4)	P(1)-Ni	2.218(3)
P(2)-Ni	2.215(3)	C(1)-Ni	1.897(7)
C(2)-Ni	1.695(8)	C(3)-P(1)	1.832(7)
C(4)-P(1)	1.834(6)	C(10)-P(1)	1.824(7)
C(16)-P(2)	1.828(7)	C(22)-P(2)	1.833(7)
C(3)-P(2a)*	1.833(7)	O(1)-C(1)	1.190(9)
O(2)-C(2)	1.176(8)	C(5)-C(4)	1.375(7)
C(9)-C(4)	1.378(8)	C(6)-C(5)	1.384(8)
C(7)-C(6)	1.361(9)	C(8)-C(7)	1.369(8)
C(9)-C(8)	1.395(8)	C(11)-C(10)	1.368(8)
C(15)-C(10)	1.382(8)	C(12)-C(11)	1.391(9)
C(13)-C(12)	1.365(10)	C(14)-C(13)	1.369(11)
C(15)-C(14)	1.377(9)	C(17)-C(16)	1.386(7)
C(21)-C(16)	1.381(8)	C(18)-C(17)	1.385(9)
C(19)-C(18)	1.366(9)	C(20)-C(19)	1.361(9)
C(21)-C(20)	1.388(8)	C(23)-C(22)	1.375(9)
C(27)-C(22)	1.383(9)	C(24)-C(23)	1.355(10)
C(25)-C(24)	1.350(14)	C(26)-C(25)	1.357(13)
C(27)-C(26)	1.411(9)		

P(1)-Ni-Ni(a)	94.1(1)	P(2)-Ni-Ni(a)	93.6(1)
C(1)-Ni-Ni(a)	46.3(1)	C(2)-Ni-Ni(a)	146.7(1)
P(2)-Ni-P(1)	106.3(2)	C(1)-Ni-P(1)	113.2(2)
C(1)-Ni-P(2)	123.5(2)	C(2)-Ni-P(1)	107.2(3)
C(2)-Ni-P(2)	104.2(3)	C(2)-Ni-C(1)	100.9(4)
Ni-C(1)-Ni(a)	87.3(4)	C(3)-P(1)-Ni	110.5(2)
C(4)-P(1)-Ni	117.6(3)	C(4)-P(1)-C(3)	104.0(3)
C(10)-P(1)-Ni	120.0(3)	C(10)-P(1)-C(3)	103.1(3)
C(10)-P(1)-C(4)	99.5(3)	C(16)-P(2)-Ni	116.7(2)
C(22)-P(2)-Ni	116.5(3)	C(22)-P(2)-C(16)	100.5(3)
C(3a)-P(2)-Ni	116.1(3)	C(3a)-P(2)-C(16)	103.1(3)
C(3a)-P(2)-C(22)	101.4(3)	O(1)-C(1)-Ni	136.3(2)
O(2)-C(2)-Ni	173.8(6)	P(1)-C(3)-P(2a)	108.9(3)
C(5)-C(4)-P(1)	121.9(5)	C(9)-C(4)-P(1)	120.0(5)
C(9)-C(4)-C(5)	118.2(6)	C(6)-C(5)-C(4)	121.2(6)
C(7)-C(6)-C(5)	120.0(6)	C(8)-C(7)-C(6)	120.1(6)
C(9)-C(8)-C(7)	119.6(6)	C(8)-C(9)-C(4)	120.8(6)
C(11)-C(10)-P(1)	125.4(5)	C(15)-C(10)-P(1)	116.1(5)
C(15)-C(10)-C(11)	118.4(6)	C(12)-C(11)-C(10)	121.1(7)
C(13)-C(12)-C(11)	119.9(8)	C(14)-C(13)-C(12)	119.4(8)
C(15)-C(14)-C(13)	120.8(8)	C(14)-C(15)-C(10)	120.4(8)
C(17)-C(16)-P(2)	117.5(5)	C(21)-C(16)-P(2)	124.9(5)
C(21)-C(16)-C(17)	117.5(6)	C(18)-C(17)-C(16)	121.1(7)
C(19)-C(18)-C(17)	120.1(7)	C(20)-C(19)-C(18)	120.1(7)
C(21)-C(20)-C(19)	120.0(7)	C(20)-C(21)-C(16)	121.3(6)
C(23)-C(22)-P(2)	122.7(6)	C(27)-C(22)-P(2)	118.7(5)
C(27)-C(22)-C(23)	118.6(6)	C(24)-C(23)-C(22)	121.1(9)
C(25)-C(24)-C(23)	121.4(10)	C(26)-C(25)-C(24)	119.4(9)
C(27)-C(26)-C(25)	120.6(9)	C(26)-C(27)-C(22)	118.8(8)

*Key to symmetry operations relating designated atoms to reference atoms at (x,y,z):

(a) -x,y,0.5-z

Table

Selected non-bonded distances (A) for [Ni2(CO)3{CH2(PPh2)2}2]

Intramolecular:

O(1)-Ni	2.878	O(2)-Ni	2.867
C(3)-Ni	3.336	H(31)-Ni	3.434
C(4)-Ni	3.471	C(9)-Ni	3.632
H(9)-Ni	3.065	C(10)-Ni	3.506
C(15)-Ni	3.862	H(15)-Ni	3.477
C(16)-Ni	3.448	C(17)-Ni	3.890
H(17)-Ni	3.610	C(22)-Ni	3.449
C(27)-Ni	3.619	H(27)-Ni	3.091
P(2)-P(1)	3.547	C(1)-P(1)	3.441
C(2)-P(1)	3.165	H(31)-P(1)	2.303
H(32)-P(1)	2.358	C(5)-P(1)	2.814
H(5)-P(1)	2.907	C(9)-P(1)	2.790
H(9)-P(1)	2.872	C(11)-P(1)	2.845
H(11)-P(1)	2.970	C(15)-P(1)	2.731
H(15)-P(1)	2.780	C(16)-P(1)	3.832
C(1)-P(2)	3.626	C(2)-P(2)	3.102
H(31)-P(2)	3.446	C(17)-P(2)	2.757
H(17)-P(2)	2.814	C(21)-P(2)	2.852
H(21)-P(2)	2.973	C(23)-P(2)	2.825
H(23)-P(2)	2.926	C(27)-P(2)	2.776
H(27)-P(2)	2.862	C(2)-C(1)	2.772
C(9)-C(1)	3.573	H(9)-C(1)	2.769
C(2)-O(1)	3.194	H(9)-O(1)	2.870
C(15)-C(2)	3.597	H(15)-C(2)	2.887
C(27)-C(2)	3.418	H(27)-C(2)	2.866
H(15)-O(2)	2.934	C(4)-C(3)	2.889
C(5)-C(3)	3.367	H(5)-C(3)	3.139
C(10)-C(3)	2.864	C(11)-C(3)	3.108
H(11)-C(3)	2.637	H(32)-H(31)	1.633
C(10)-H(31)	2.942	C(11)-H(31)	2.980
H(11)-H(31)	2.449	C(21)-H(31)	3.173
C(4)-H(32)	2.968	C(5)-H(32)	3.021
H(5)-H(32)	2.577	C(10)-H(32)	2.951
C(11)-H(32)	2.879	H(11)-H(32)	2.258
H(5)-C(4)	2.028	C(6)-C(4)	2.404
C(7)-C(4)	2.777	C(8)-C(4)	2.411
H(9)-C(4)	2.033	C(10)-C(4)	2.792
C(15)-C(4)	3.355	H(6)-C(5)	2.042
C(7)-C(5)	2.377	C(8)-C(5)	2.740
C(9)-C(5)	2.361	C(10)-C(5)	3.161
C(6)-H(5)	2.034	H(6)-H(5)	2.334
C(10)-H(5)	2.872	C(11)-H(5)	3.051
H(7)-C(6)	2.019	C(8)-C(6)	2.366
C(9)-C(6)	2.743	C(7)-H(6)	2.020
H(7)-H(6)	2.320	H(8)-C(7)	2.029
C(9)-C(7)	2.389	C(8)-H(7)	2.026
H(8)-H(7)	2.330	H(9)-C(8)	2.046
C(9)-H(8)	2.053	H(9)-H(8)	2.350
H(11)-C(10)	2.021	C(12)-C(10)	2.402
C(13)-C(10)	2.777	C(14)-C(10)	2.394
H(15)-C(10)	2.036	C(17)-C(10)	3.512
H(12)-C(11)	2.050	C(13)-C(11)	2.385
C(14)-C(11)	2.730	C(15)-C(11)	2.362
C(12)-H(11)	2.042	H(12)-H(11)	2.347
H(13)-C(12)	2.028	C(14)-C(12)	2.360
C(15)-C(12)	2.744	C(13)-H(12)	2.023
H(13)-H(12)	2.330	H(14)-C(13)	2.025
C(15)-C(13)	2.387	C(14)-H(13)	2.029

H(14)-H(13)	2.328	H(15)-C(14)	2.033
C(15)-H(14)	2.029	H(15)-H(14)	2.327
C(17)-C(15)	3.535	H(17)-C(16)	2.038
C(18)-C(16)	2.413	C(19)-C(16)	2.785
C(20)-C(16)	2.413	H(21)-C(16)	2.032
C(22)-C(16)	2.815	C(23)-C(16)	3.082
H(23)-C(16)	2.677	H(18)-C(17)	2.041
C(19)-C(17)	2.384	C(20)-C(17)	2.742
C(21)-C(17)	2.366	C(22)-C(17)	3.278
C(23)-C(17)	3.415	H(23)-C(17)	3.101
C(18)-H(17)	2.037	H(18)-H(17)	2.336
C(22)-H(17)	3.062	H(19)-C(18)	2.026
C(20)-C(18)	2.363	C(21)-C(18)	2.739
C(19)-H(18)	2.025	H(19)-H(18)	2.329
H(20)-C(19)	2.019	C(21)-C(19)	2.381
C(20)-H(19)	2.018	H(20)-H(19)	2.317
H(21)-C(20)	2.038	C(21)-H(20)	2.045
H(21)-H(20)	2.339	H(23)-C(22)	2.028
C(24)-C(22)	2.378	C(25)-C(22)	2.770
C(26)-C(22)	2.406	H(27)-C(22)	2.047
H(24)-C(23)	2.007	C(25)-C(23)	2.359
C(26)-C(23)	2.722	C(27)-C(23)	2.372
C(24)-H(23)	2.008	H(24)-H(23)	2.294
H(25)-C(24)	2.010	C(26)-C(24)	2.337
C(27)-C(24)	2.738	C(25)-H(24)	2.004
H(25)-H(24)	2.301	H(26)-C(25)	2.010
C(27)-C(25)	2.405	C(26)-H(25)	2.022
H(26)-H(25)	2.317	H(27)-C(26)	2.071
C(27)-H(26)	2.066	H(27)-H(26)	2.379

Intermolecular:

P(1)-Ni(a)	3.550	P(2)-Ni(a)	3.535
C(1)-Ni(a)	1.897	O(1)-Ni(a)	2.878
C(2)-Ni(a)	4.142	C(3)-Ni(a)	3.441
H(31)-Ni(a)	3.717	P(2)-P(1a)	2.982
C(1)-P(1a)	3.441	C(22)-P(1a)	3.837
C(1)-P(2a)	3.626	C(3)-P(2a)	1.833
H(31)-P(2a)	2.348	H(32)-P(2a)	2.463
C(4)-P(2a)	3.682	H(26)-O(1b)	2.877
C(7)-O(2c)	3.351	H(7)-O(2c)	2.660
C(8)-O(2c)	3.459	H(8)-O(2c)	2.885
H(18)-O(2d)	2.710	H(12)-O(2e)	2.885
C(16)-C(3a)	2.868	C(21)-C(3a)	3.125
H(21)-C(3a)	2.664	C(22)-C(3a)	2.837
C(23)-C(3a)	3.474	C(16)-H(31a)	2.881
C(21)-H(31a)	2.749	H(21)-H(31a)	2.089
C(22)-H(32a)	2.916	C(27)-C(4a)	3.495
C(20)-C(5f)	3.562	H(20)-C(5f)	3.129
C(19)-H(5f)	2.856	H(19)-H(5f)	2.638
C(20)-H(5f)	2.877	H(20)-H(5f)	2.673
H(20)-C(6f)	3.175	C(13)-H(7g)	3.070
C(27)-C(9a)	3.456	H(27)-C(9a)	3.001
H(13)-H(9e)	2.752	C(25)-C(14d)	3.554
C(24)-H(14d)	3.062	C(25)-H(14d)	2.773
C(26)-H(14d)	3.031	H(24)-C(20f)	3.032
H(24)-H(20f)	2.464	C(25)-C(25h)	3.323
H(25)-C(25h)	2.761	H(25)-H(25h)	2.397

Key to symmetry operations relating designated atoms to reference atoms at (x,y,z):

(a) -x,y,0.5-z	(b) -x,-y,1.0-z
(c) x,-y,-0.5+z	(d) 0.5-x,0.5-y,1.0-z

(e) 0.5-x,0.5+y,0.5-z
(f) x,1.0-y,0.5+z
(g) 0.5-x,0.5-y,-z
(h) -x,y,1.5-z